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A CRITICAL EVALUATION OF REACTIONS AND RATE CONSTANTS ASSOCIATED WITH THE FORMATION AND DESTRUCTION OF N_2O IN COMBUSTION SYSTEMS

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EXECUTIVE SUMMARY

This report reviews papers published to date on the kinetics of reactions associated with the formation and destruction of N_2O in combustion systems. Particular attention is paid to the reactions that might be significant under conditions prevalent in fluidized bed combustion. A total of 398 papers were reviewed. The following subjects are covered: 1) gas phase reactions of N_2O with various molecules, atoms, and radicals; 2) gas phase reactions contributing to formation of N_2O; 3) catalytic reactions of NO with NH_3, CO, H_2, and carbonaceous materials over char, limestone, quartz, $CaSO_4$, metal, and metal oxide surfaces; 4) the thermal $DeNO_x$ process; 5) oxidation and dissociation of NH_3; 5) artifact in measurements of N_2O.

All published rate constants for the reactions are tabulated and presented in Arrhenius plots so as to provide clear comparisons of the results from various authors. The mechanisms proposed for these reactions are summarized and critically evaluated. The methods used in each investigation are discussed. An assessment of the reliability of the data is given.

Based on the summaries and evaluations, the following conclusions are presented:

1) In combustion of coal or oil, HCN and NCO are important species for N_2O formation. The source of HCN may be either devolatilization, or a char gasification. The formation of N_2O from HCN occurs through reaction of HCN with O to form NCO followed by reaction of NCO with NO to form N_2O. In order to model N_2O formation, accurate rate measurements for the reactions of HCN with O and NCO with NO over the temperature range applicable in combustion is required.

2) The rate constants for reactions of N_2O with H and O and for the dissociation of N_2O are well established. These rate constants are sufficiently large for destruction of N_2O at flame temperatures above 1000K. Thus, N_2O formed in combustion systems likely results from the post flame zone where the temperature is below 1000K.

3) Low temperature (400 - 800K) reduction of NO by NH_3 and CO over metal and metal oxide surfaces produces large amounts of N_2O. Lack of experimental data hampers the evaluation of the importance of these reactions.

4) Since char, limestone, quartz, and $CaSO_4$ are often present in fluidized bed combustors, the catalytic effects of these materials on the formation and destruction of N_2O could be important. However, evaluation of the importance of these reactions is hampered by lack of data on these reactions.

5) The formation of N_2O in mixtures of $NO/SO_2/H_2O/O_2$ in sample cells has been clearly identified as a source of error in N_2O field measurements. No measurements have been made of this reaction at increased temperatures or at various concentration ratios. A detailed study of this system is required in order to determine if similar reactions may affect formation of N_2O in combustion or post combustion gases.

Abrégé

Ce rapport examine les articles publiés à ce jour sur la cinétique des réactions associées à la formation et à la destruction de N_2O dans les systèmes de combustion. Il s'intéresse notamment aux réactions pouvant s'avérer importantes dans les conditions qui règnent lors de la combustion des fournaises à lit fluidisé. Un total de 398 articles ont été étudiés. Les sujets suivants sont traités: 1) les réactions de la phase gazeuse de N_2O pour des molécules, des atomes et des radicaux variés; 2) les réactions de la phase gazeuse qui contribuent à la formation de N_2O; 3) les réactions catalytiques de NO avec NH_3, CO, H_2 et des matériaux carbonés sur des surfaces en charbon, en pierre calcaire, en quartz, en $CaSO_4$, en métal et en oxyde métallique; 4) le processus thermique $DeNO_x$; 5) l'oxydation et la dissociation de NH_3; 6) l'altération résultant du mesurage de N_2O.

Toutes les constantes de taux des réactions qui ont été publiées sont classifiées et présentées sous forme de diagrammes d'Arrhenius, afin de permettre d'établir des comparaisons claires entre les résultats des différents auteurs. Les mécanismes proposés pour ces réactions sont résumés et évalués de facon critique. Les méthodes utilisées dans chaque recherche sont discutées. Une évaluation de la fiabilité des données est fournie.

Ces résumés et évaluations permettent de formuler les conclusions suivantes:

1) Dans la combustion du charbon ou du pétrole, HCN et NCO sont des facteurs importants pour la formation de N_2O. La source de HCN peut être la dévolatilisation ou la gazéification du charbon. La formation de N_2O à partir de HCN est causée par la réaction de HCN avec O pour former NCO, laquelle est suivie de la réaction de NCO avec NO pour former N_2O. Pour pouvoir préparer un modèle de la formation de N_2O, il est essentiel que les taux des réactions de HCN avec O et de NCO avec NO, dans la zone des températures applicables lors de la combustion, soient mesurés avec exactitude.

2) Les constantes de taux des réactions de N_2O avec H et O et de la dissociation de N_2O sont bien établies. Ces constantes de taux sont suffisamment importantes pour assurer la destruction de N_2O à des températures de flamme supérieures à 1000K. Par conséquent, le N_2O formé dans les systèmes de combustion provient en toute probabilité de la zone située au-delà de la flamme, où la température est inférieure à 1000K.

3) La réduction à basse température (400 - 800K) de NO par NH_3 et CO sur des surfaces en métal et en oxyde métallique produit de grandes quantités de N_2O. L'absence de données d'expériences rend difficile l'évaluation de l'importance de ces réactions.

4) Puisque le charbon, la pierre calcaire, le quartz et le $CaSO_4$ sont souvent présents dans les fournaises à lit fluidisé, les effets catalytiques de ces matériaux sur la formation et la destruction de N_2O pourraient être importants. Toutefois,

l'évaluation de l'importance de ces réactions est rendue difficile par l'absence de données sur ces réactions.

5) La formation de N_2O en mélanges de $NO/SO_2/H_2O/O_2$ dans des échantillons d'éléments a été clairement identifiée comme une source d'erreurs dans les mesurages de N_2O effectués sur le terrain. Aucun mesurage n'a été fait de cette réaction à des températures plus élevées ou à des taux de concentration variés. Une étude détaillée de ce système s'avère nécessaire pour déterminer si des réactions similaires risquent d'affecter la formation de N_2O dans les gaz de combustion ou les gaz qui se produisent après la combustion.

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TABLE OF SYMBOLS AND ABBREVIATIONS

M	Mass
A	Pre-exponetial Factor
k	Rate Constant
E	Activation Energy
T	Temperature
R	Gas Constant
AERROR	Error in Pre-exponential Factor
KERROR	Error in Rate Constant
AVMD	Absolute Rate Data Measured Directly
BGAS	Bath Gas
CE	Critical Evaluation
CHEMIL	Chemical Luminescence
EP	End Product Analysis
E/R	Activation Energy Divided by Gas Constant
ERERR	Error in E/R
ESTIM	Estimated Data
FD	Flow Discharge
FIT	Fitting to A Complex Mechanism
FP	Flash Photolysis
FT	Flow Tube
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatograph
HTP	High Temperature Photochemistry
IR	Infrared Spectroscopy

IR E	Infrared Emission
LF	Low Flow Reactor
LIF	Laser Induced Fluorescence
LMR	Laser Magnetic Resonance
LP	Laser Photolysis
LS	Laser Schlieren
MS	Mass Spectroscopy
RAC	Rapid Adiabatic Compression
RECOM	Recommended Rate Data
RELAT	Rate Data obtained relative to a Reference Reaction
RF	Resonance Fluorescence
RT	Real Time Measurement
S/LF	Static and Low Flow Reactor
ST	Shock Tube
T	Thermolysis
TEMP	Temperature
TOFMS	Time of Flight Mass Spectroscopy
ULMD	Upper limit Measured Directly
V/UV A	Vis/UV Absorption
V/UV E	Vis/UV Emission

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A CRITICAL EVALUATION OF REACTIONS AND RATE CONSTANTS ASSOCIATED WITH THE FORMATION AND DESTRUCTION OF NITROUS OXIDE IN COMBUSTION SYSTEMS

INTRODUCTION

Nitrous oxide (N_2O) is a molecule of considerable practical and theoretical interest. It is often used as an oxidant, more specifically, as a source of electronically excited oxygen atoms in the study of reactions of oxygen atoms with other species[1]. In order to analyze the experimental data from these studies, reliable data for the reactions of N_2O with excited oxygen atoms was necessary. Of theoretical interest is the fact that nitrous oxide is the smallest molecule whose decomposition involves two potential energy surfaces of different multiplicities. In addition, the entire unimolecular fall-off region is experimentally accessible, making it attractive for testing various theories. For these reasons, many reactions of nitrous oxide, such as, thermal decomposition, photolysis and reactions with oxygen and hydrogen, have been studied extensively. Various experimental techniques, including shock tube, flash and static photolysis, flow discharge techniques, atomic resonance fluorescence, and UV/infrared emission and absorption spectroscopy, have been widely used to obtain rate data for these reactions.

Recently, the environmental effects of N_2O have become a concern. The transport of nitrous oxide across the tropopause is a major source of stratospheric nitric oxide (NO). This occurs when the reaction of N_2O with singlet oxygen produces NO,

$$N_2O + O(^1D) \rightarrow 2NO$$

which enters into the ozone destruction chemistry cycle[2,3,4]. In fact, if one integrates over the whole atmosphere over all seasons, one finds that NO is responsible for 65-70% of the destruction of O_3 in the atmosphere. A similar calculation for Cl indicates that Cl is responsible for approximately 10%. Nitrous oxide is also an efficient absorber of infrared radiation and thus is a potential "greenhouse-effect" gas[5,6]. The global mean concentration of nitrous oxide, presently 303 ppb, is increasing at a rate of 0.55 ppb per year according to Weiss[7]. Uncertainties in the source, sink and accumulation terms have, however, prevented a firm identification of the importance of the various sources. Hao et al.[8] estimated that combustion of fossil fuel releases 3.2×10^6 tons of N_2O (as N)y^{-1} at present, with 83% of this derived from burning of coal in large industrial boilers. Kramlich et al.[9] also have observed significant N_2O emission from coal and oil burning power plants, but they pointed out that there still exist large uncertainties on the mechanism of formation of N_2O in combustion processes. Contrary to the situation for NO and NO_2, reactions of N_2O have not been investigated extensively, with the intent to provide information on its formation and destruction in combustion processes.

Fundamental to the prediction and control of emission of N_2O in large scale commercial boilers is a detailed understanding of the rates and mechanisms of the reactions that contribute to the production and destruction of N_2O. It is thus important to review the published rate data of reactions of N_2O.

Although several reviews have included rate data on N_2O reactions[10-15], they have been primarily concerned with elementary reactions of atmospheric interest. Baulch et al.[10] have summarized some rate data on the reactions of nitrous oxide in their critical evaluation of kinetic data for high temperature reactions. More recently, DeMore et al.[11] presented a recommended set of rate constants and photochemical cross sections for use in modelling of stratospheric processes and include some data on N_2O reactions. However, no comprehensive review specific to reactions of N_2O has yet been produced.

In this report, we have attempted to produce a concise up to-date comprehensive review of the kinetics of reactions of nitrous oxide. An emphasis has been placed on the kinetic parameters and mechanisms of the various reactions related to the formation and destruction of N_2O in combustion processes. The report is divided into two parts. Part I reviews elementary reactions while Part II reviews global reactions including heterogeneous reactions.

PART I. ELEMENTARY REACTIONS

1-1. DECOMPOSITION OF NITROUS OXIDE

(1) Thermal decomposition of N_2O

It is generally accepted[10] that the primary step leading to thermal decomposition of N_2O is reaction (1-1.1),

$$N_2O + M \longrightarrow N_2 + O + M \qquad (1\text{-}1.1)$$

followed by two subsequent reactions (1-1.2) and (1-1.3):

$$N_2O + O \longrightarrow N_2 + O_2 \qquad (1\text{-}1.2)$$

$$N_2O + O \longrightarrow NO + NO \qquad (1\text{-}1.3)$$

Early studies of reaction (1-1.1) were based on static thermal systems whereas more recent studies (since early 70's) have centred on exploiting high temperature shock tube techniques[16-31]. Many methods have been used to monitor the decay of N_2O, including TOF mass spectrometry[18,19,24,25], Vis and UV absorption and emission spectroscopy[21,23,27,29,31,32], IR absorption and emission spectroscopy[33-35], chemiluminescence[36], and gas chromatography[28,37,38]. After a multitude of investigations spanning several generations of investigators, data have been published with total pressure from several torr to 300 atm and temperatures from 850K to 3345K. A summary of published kinetic parameters of reaction (1-1.1) is given in Table 1-1.1 and the Arrhenius plots of the rate constants for reaction (1-1.1) with M = He, Ne, Ar, Kr, N_2O are given in Figure (1-1.1)-(1-1.5), respectively.

Even though reaction (1-1.1) had been investigated extensively, a quantitative understanding was still somewhat unsatisfactory before 1973 [28]. One complication results from the subsequent reactions (1-1.2) and (1-1.3). Most experimentally measured rate constants refer to the rate of disappearance of N_2O, k_{obs}, which corresponds to $2k_{1-1.1}$ and $k_{1-1.1}$ according to whether or not a steady state concentration of atomic oxygen could be established before the observation period. This problem is aggravated by an uncertainty in the values of $k_{1-1.2}$ and $k_{1-1.3}$[17]. Olschewski et al.[35], from a shock tube study, reported that at 2000K and above, k_{obs} was a factor of two less when a very dilute mixture of N_2O/Ar (0.02%) was studied, than when a 0.1% N_2O/Ar or higher concentration was studied. It is possible that they observed $k_{1-1.1}$ directly at this very low concentration. Fenimore and Jones[39] found that $k_{1-1.1}$ was about $(0.55-0.6)k_{obs}$ for their temperature range of 1780-2790K. Borisov[18] obtained approximate analytical solutions to the non-linear differential kinetic equations describing the N_2O/Ne dissociation. Using shock tube-TOF mass spectrometric techniques to monitor $[N_2]$, $[O_2]$, [NO], and $[N_2O]$

Table 1-1.1 Summary of the Rate Parameters for Reaction N_2O + M --> N_2 + O + M

BGAS	PRESSURE (torr)	TEMP(K)	E/R(K)	ERROR%	LogA cm^3/mole*s	AERROR (%)	Logk cm^3/mole*s	METHOD	DATATYPE	YEAR	REF
He	231-541	1600-2320	28181		15.246	25.0		ST,V/UV A	AVMD,RT	1980	31
He	112-740	2000					9.061	ST,V/UV A	AVMD,RT	1979	21
Ne	1246	1500-2500	21940	50.0	13.403	50.0		CE,	RECOM	1973	28
Ne	228	1600-2100	20631		13.250			ST,TOFMS	AVMD,EP	1970	19
Ne	0.55	1815					8.278	ST,TOFMS	FIT ,RT	1968	18
Ne	228	1820					8.079	ST,TOFMS	FIT ,EP	1969	24
Ne	228	1820			8.341			ST,TOFMS	FIT ,EP	1969	24
Ne	236-296	1880-2360	26418		14.227			ST,TOFMS	FIT ,EP	1965	25
Ne	646	1890					8.505	ST,TOFMS	FIT ,RT	1968	18
Ne	357-441	1920-2350	25418		14.195			ST,TOFMS	FIT ,EP	1965	25
Ne	112-744	2000					9.602	ST,V/UV	AVMD,RT	1979	21
Ne	479	2010					8.897	ST,TOFMS	FIT ,RT	1968	18
Ne	228	2015					8.956	ST,TOFMS	FIT ,EP	1969	24
Ne	266	2029					9.124	ST,TOFMS	FIT ,RT	1968	18
Ne		2050					8.764	ST,TOFMS	FIT ,RT	1968	18
Ne	228	2150					8.956	ST,TOFMS	FIT ,EP	1969	24
Ne	228	2170					8.968	ST,TOFMS	FIT ,EP	1969	24
Ne		2180					9.218	ST,TOFMS	FIT ,RT	1968	18
Ne	228	2205					8.852	ST,TOFMS	FIT ,EP	1969	24
Ne	228	2205					8.852	ST,TOFMS	FIT ,EP	1969	24
Ne		2330					9.380	ST,TOFMS	FIT ,RT	1968	18
Ne	228	2350					9.341	ST,TOFMS	FIT ,EP	1969	24
Ne	228	2370					9.356	ST,TOFMS	FIT ,EP	1969	24
Ne	228	2420					9.494	ST,TOFMS	FIT ,EP	1969	24
Ne	228	2550					9.549	ST,TOFMS	FIT ,EP	1969	24
Ne	228	2600					9.652	ST,TOFMS	FIT ,EP	1969	24
Ar	30-200	1000-2000	28684	3.0	14.700			ST,V/UV A	AVMD,RT	1972	32
Ar		1000-3000	29187		14.672			ST,CHEMIL	FIT,RT	1972	36
Ar		1323					4.758	RAC,IR	FIT ,EP	1966	33
Ar		1357					5.305	RAC,IR	FIT ,EP	1966	33
Ar		1390					5.324	RAC,IR	FIT ,EP	1966	33
Ar	8.7-22E4	1410-2080	29940		11.140			ST,IR E	FIT ,RT	1966	35
Ar		1428					5.699	RAC,IR	FIT ,EP	1966	33
Ar	608-9120	1480-2530	29186		14.672			ST,IR E	FIT ,RT	1966	34
Ar	1.5-15E3	1500-2500	30695		15.010			ST,V/UV A	FIT ,RT	1964	26
Ar	1246	1500-2500	29816	50.0	14.672	25.0		CE,	RECOM,	1973	28
Ar	4256-5092	1530-1820	30192		14.859			ST,V/UV A	FIT ,RT	1963	27
Ar	1.5-16E3	1640-2195	28028		13.894			ST,IRE/UV	FIT ,RT	1964	22
Ar	2508-3040	1665-1919	28582		14.496			ST,UV A	FIT ,RT	1967	20
Ar	1292-3496	1685-2560	27660	5.0	14.569	73.5		ST,V/UV E	FIT ,RT	1980	29
Ar	130-300	1700-2500	29924	10.0	14.968	24.0		ST,V/UV A	FIT,RT	1985	23
Ar	8.1-10E3	1728-2190	28028		13.926			ST,IRE/UV	FIT ,RT	1964	22
Ar	2052-2432	1738-2060	25864		13.821			ST,IRE/UV	FIT ,RT	1964	22
Ar	3040-3496	1748-2020	26368		13.859			ST,IRE/UV	FIT ,RT	1964	22
Ar	304-380	1815-3365	25806		14.152			ST,IR.	FIT, RT	1977	48
Ar	186-435	1820-3170	28181		14.643			ST,V/UV A	AVMD,RT	1980	31

Table 1-1.1.Continued

BGAS	PRESSURE (torr)	TEMP(K)	E/R(K)	ERROR%	LogA cm3/mole*s	AERROR (%)	Logk cm3/mole*s	METHOD	DATATYPE	YEAR	REF
Ar	60-74	1850-2535	28625		14.894			ST,V/UV A	FIT,RT	1975	43
Ar	60-74	1850-2535	28181	1.8	14.470			ST,V/UV	AVMD,RT	1975	43
Ar	1353	1850-2550	30800		14.161			ST,V/UV E	AVMD,RT	1985	49
Ar	1520-1778	1908-2160	25908		13.694			ST,IRE/UV	FIT ,RT	1964	22
Ar	37-77	1950-3075	24476	2.0	14.061			ST,IR	AVMD,RT	1976	44
Ar	37-77	1950-3075	25859		14.292			ST,IR	FIT,RT	1976	44
Ar	112-744	2000					8.322	ST,V/UV A	AVMD,RT	1979	21
Ar		2000					12.124			1982	50
Kr	372	1300-1950	22192		13.100			ST,GC	AVMD,EP	1973	38
Kr	372	1400-2000	20492	8	12.490			ST,GC	AVMD,EP	1971	37
Kr	372	1400-2000	24553	9	13.130			ST,GC	AVMD,EP	1971	37
Kr	1246	1750-2800	20480	20	12.859	20.0		CE	RECOM,	1973	28
Kr	152-304	1780-2790	20480		12.875			ST,TOFMS	FIT ,EP	1969	51
Kr	112-744	2000					8.217	ST,V/UV A	AVMD,RT	1979	21
Xe	112-744	2000					8.146	ST,V/UV A	AVMD,RT	1979	21
N2O	6.85-100	1000-3000	27677		14.961	1.0		S/LF,GC	FIT,EP	1985	52
N2O	40	1670-1980	28432		14.114	30.7		FLAME,MS	AVMD,EP	1977	106
N2O	15-61	841-1052	29387		15.452			CE	RECOM,	1951	53
N2O	125	850-1050	29890	20	15.452	20.0		CE	RECOM,	1973	28
N2O	996	993					2.106	S/LF	AVMD,EP	1955	54
N2O	502	993					2.164	S/LF	FIT ,EP	1955	54
N2O	20	993					2.773	S/LF	FIT ,EP	1955	54
N2O	198	993					2.295	S/LF	FIT ,EP	1955	54
N2O	10	993					2.884	S/LF	FIT ,EP	1955	54
N2O	296	993					2.229	S/LF	FIT ,EP	1955	54
N2O	403	993					2.190	S/LF	FIT ,EP	1955	54
N2O	40	993					2.638	S/LF	FIT ,EP	1955	54
N2O	99	993					2.433	S/LF	FIT ,EP	1955	54
O2	1672-2280	1545-2155	25160		13.758			ST,IRE/UV	FIT ,RT	1964	22
O2	1064-1520	1550-2175	24254		13.619			ST,IRE/UV	FIT ,RT	1964	22
CO	180-1710	1415-2820	28181		15.120	33.3		ST,V/UV A	AVMD,RT	1980	31
CF4	112-744	2000					9.114	ST,V/UV A	AVMD,RT	1979	21
N2	5320-7600	1250-1800	26571		11.146			ST,V/UV A	AVMD,RT	1972	30

Figure 1-1.1. N2O + He --> N2 + O + He

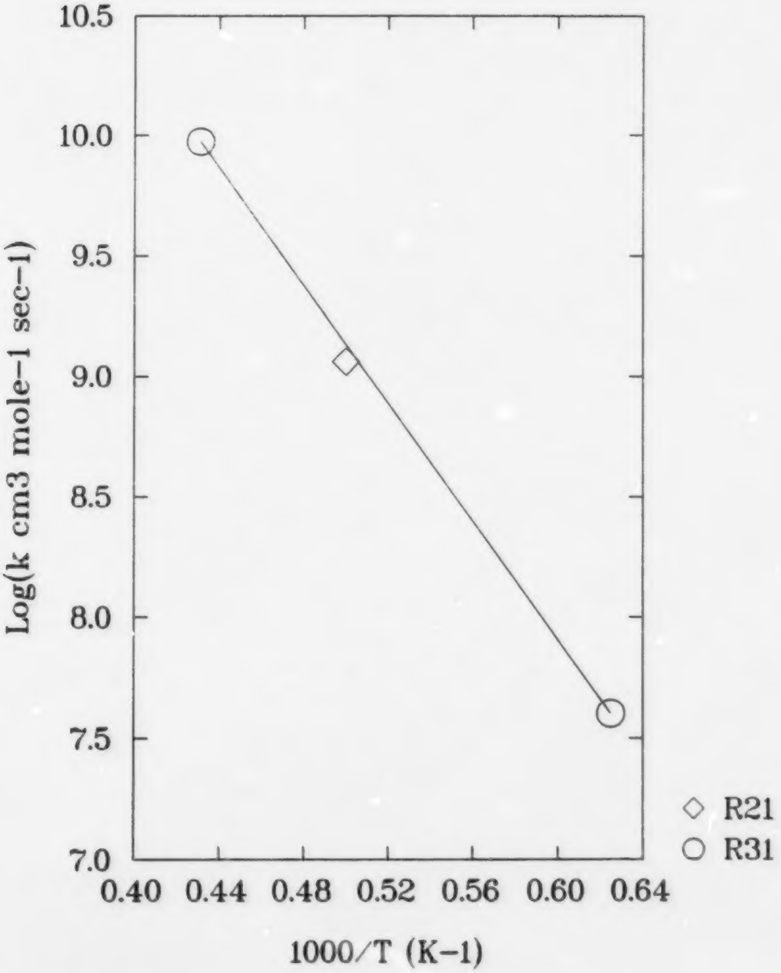


Figure 1-1.2. N2O + Ne --> N2 + O + Ne

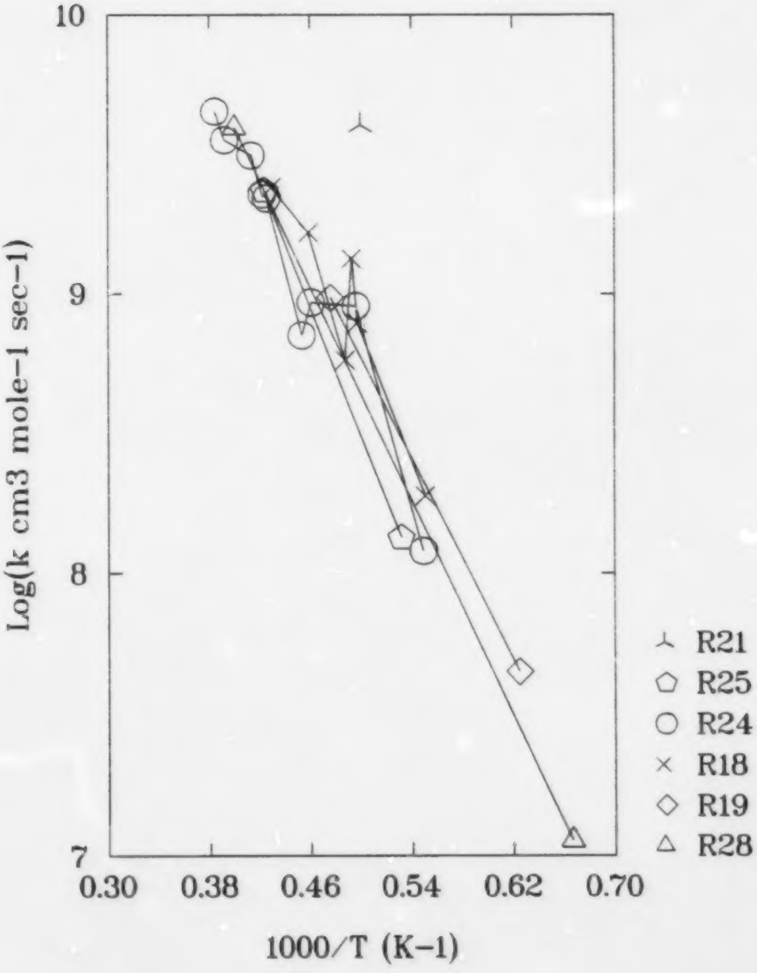


Figure 1-1.3a. N2O + Ar --> N2 + O + Ar (1)

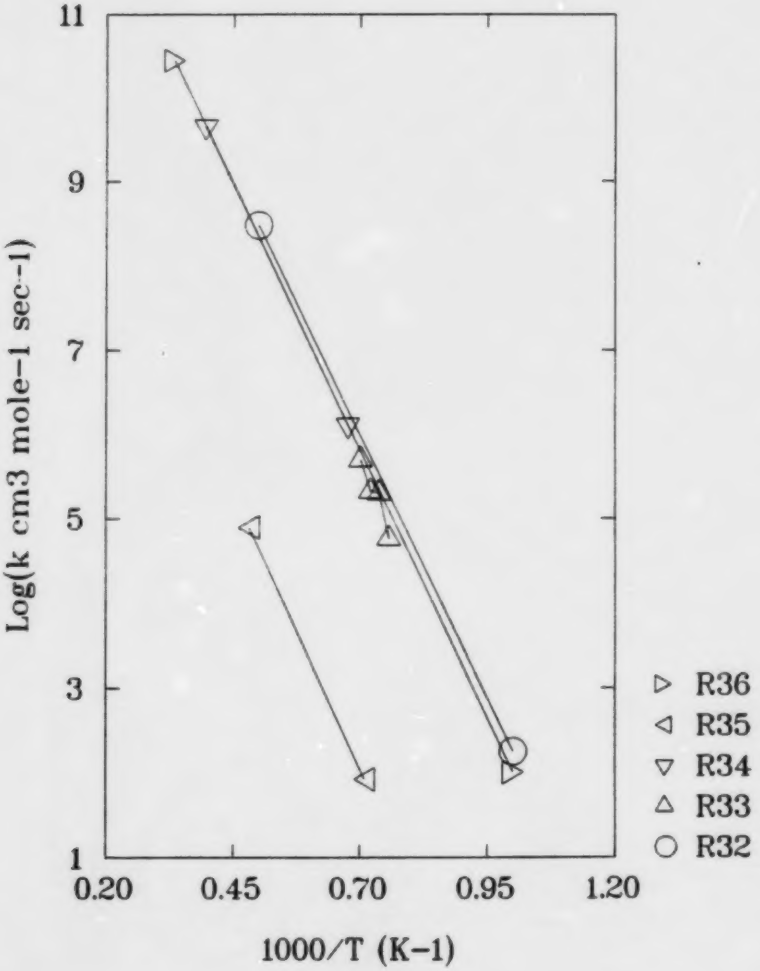


Figure 1–1.3b. N2O + Ar --> N2 + O + Ar (2)

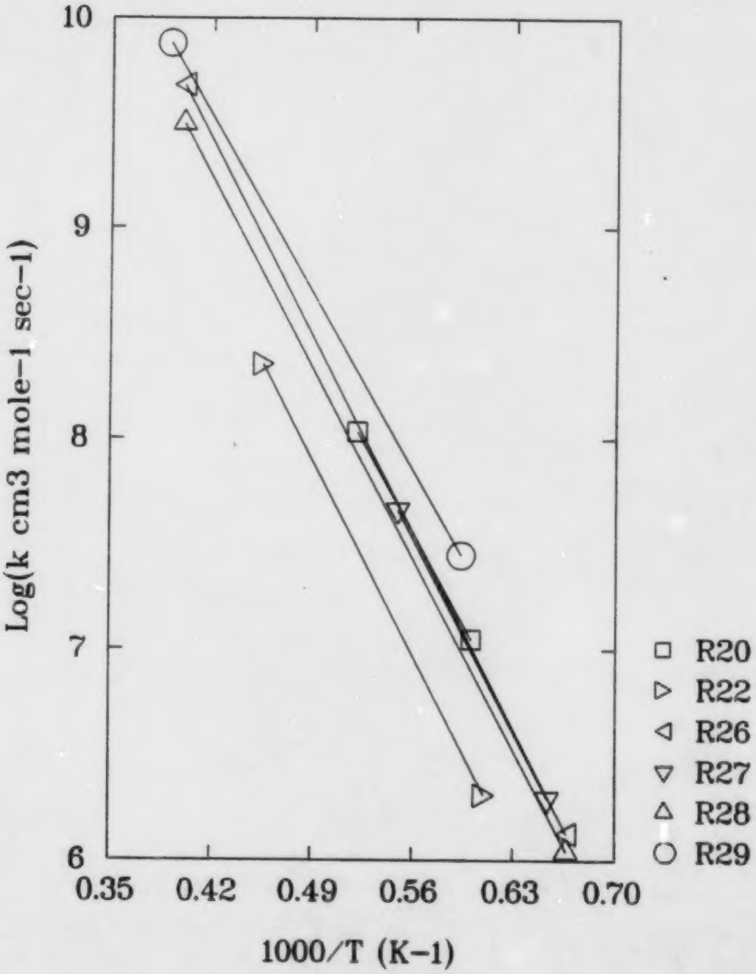


Figure 1-1.3c. N2O + Ar --> N2 + O + Ar (3)

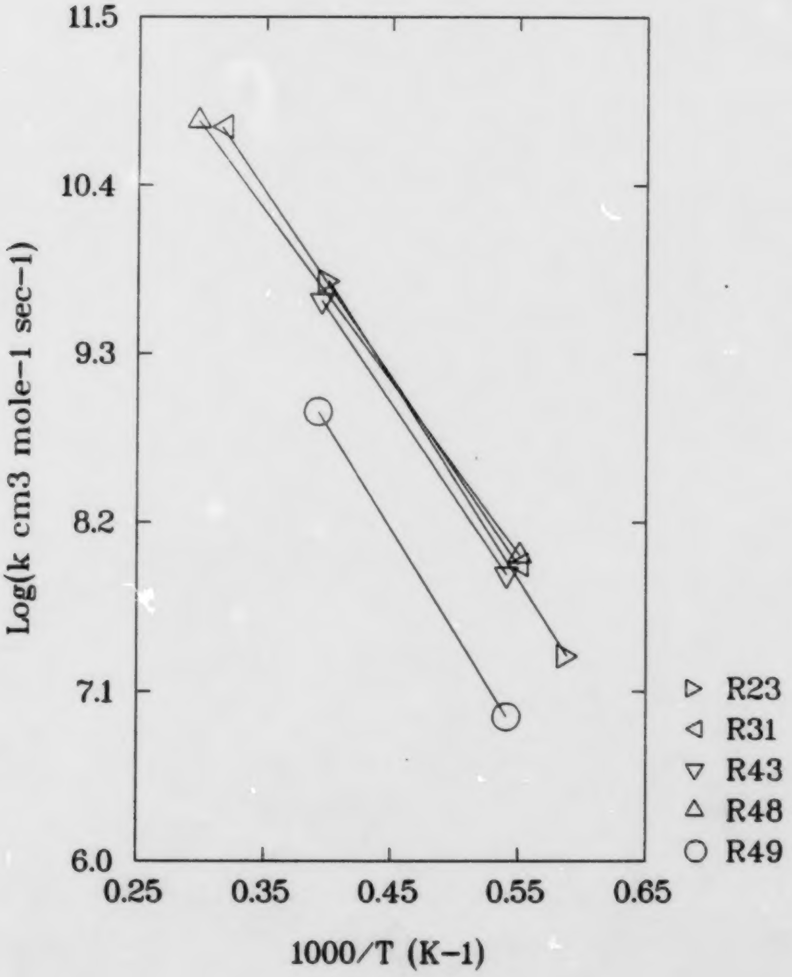


Figure 1-1.3d. N2O + Ar --> N2 + O + Ar (4)

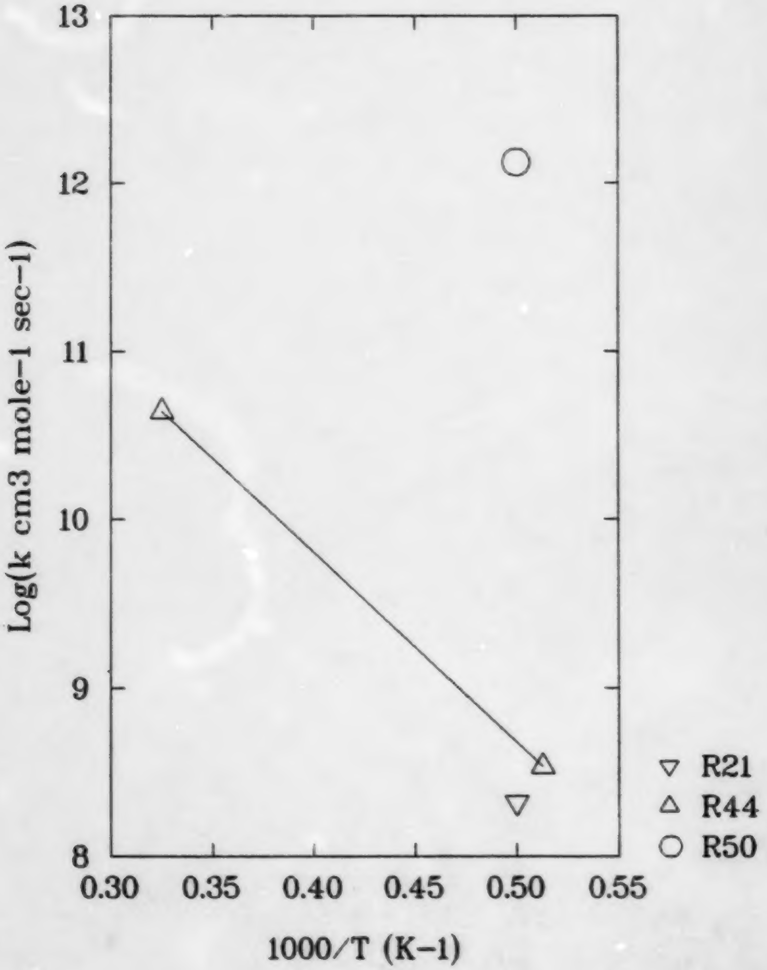


Figure 1–1.4. N20 + Kr —> N2 + O + Kr

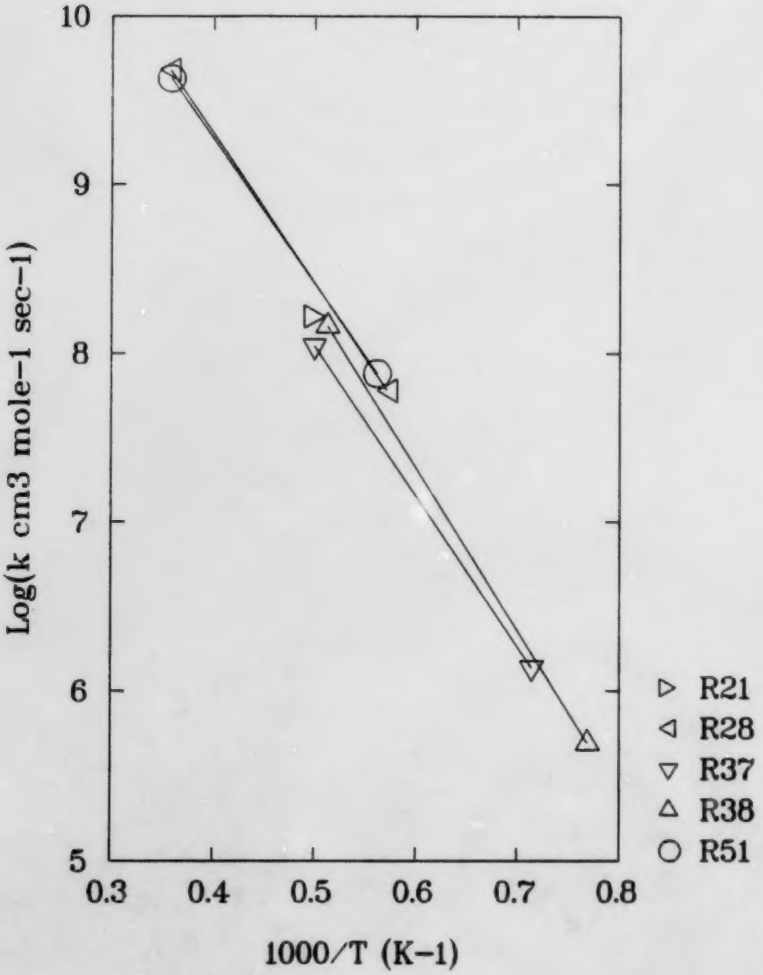
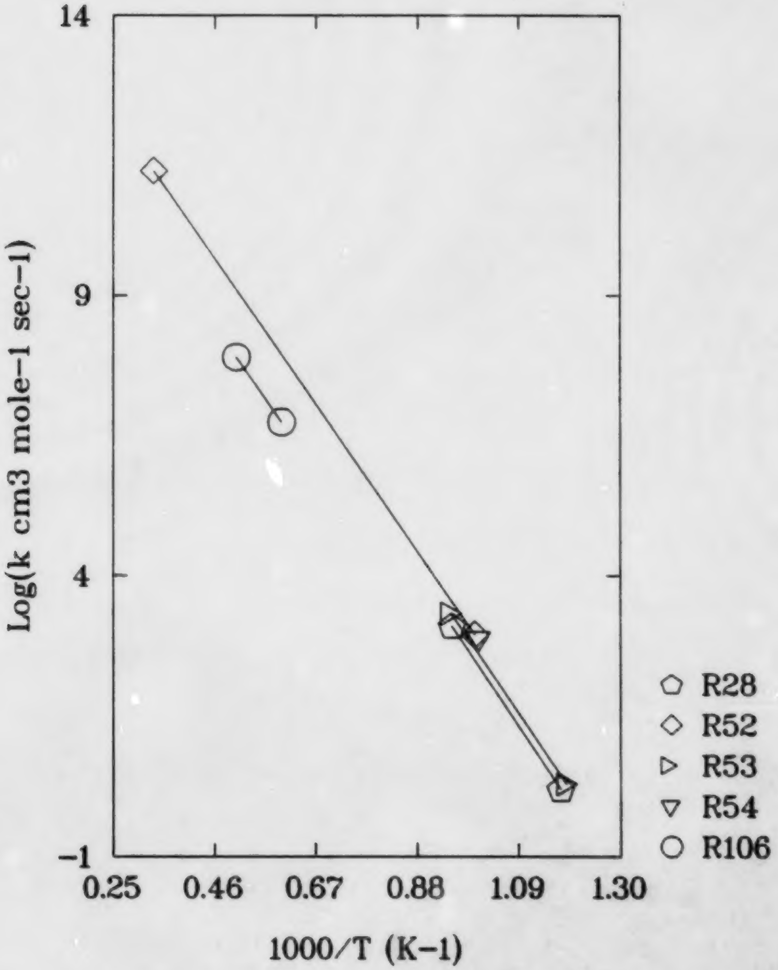


Figure 1–1.5. N20 + N20 --> N2 + 0 + N20



he derived $k_{1-1.1}$, $k_{1-1.2}$, and $k_{1-1.3}$. Gutman et al.[40] did not observe O-atoms and contributed this to a rapid attainment of a low steady-state O-atom concentration. However, Clark et al.[19] have calculated that the O atom concentration for N_2O/Ne mixtures at <2100K can be described as a linear function of time, indicating insufficient time for a steady state to be established in these studies.

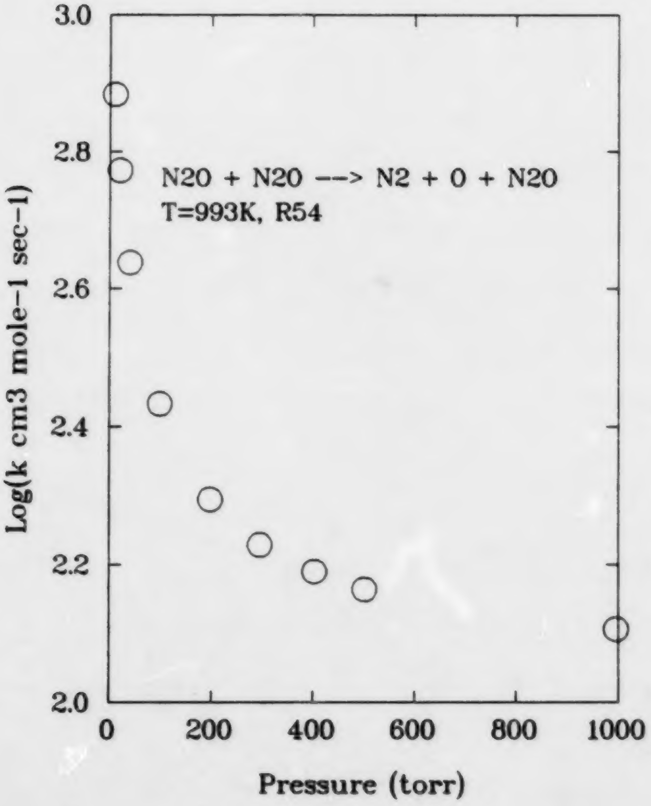
At low temperatures the formation of NO is evidence for a contribution from reaction (1-1.3). In 1956, Kaufman et al.[41] found large amounts of NO formed in the initial stage of the dissociation of N_2O at low temperature. As a result, in the 70's, it was generally accepted that the contribution from reactions (1-1.2) and (1-1.3) are of some importance at all temperatures,[28] and many investigations were carried out to obtain more information about the decomposition of N_2O using various techniques to measure the concentration of species in addition to N_2O. Blair[42] attempted to monitor the O-atom concentration by adding CO to the system and detecting the "flame band" emission resulting from the radiative recombination of O and CO. However, he did not obtain satisfactory data because background emission resulting from an unidentified source precluded kinetic analysis of the data. Baber and Dean[43] studied the dissociation of N_2O/Ar mixtures with and without added CO by monitoring both infrared and ultraviolet emission behind reflected shock waves and obtained $k_{1-1.1}$, $k_{1-1.2}$, and $k_{1-1.3}$ by fitting data to numerical integration of the reaction mechanism. Dean[44] obtained further information on reactions (1-1.2) and (1-1.3) by the addition of small amounts of H_2 to N_2O/Ar mixtures, which opened a new channel for N_2O decay. He found that agreement between experimental data and numerical integration of the mechanism was obtained only when low values were assigned to $k_{1-1.2}$ and $k_{1-1.3}$. At present, most of the values of $k_{1-1.1}$ are in agreement within a factor of approximately 2 to 3 in the pressure range of 30 torr to 20 atm. However, the reported activation energies scatter between 40 and 61 kcal/mole.

The relative efficiency of different third bodies, such as Ar, He, Ne, Kr, Xe, N_2O, CO_2, CF_4, and SO_2, in the decomposition of N_2O has also been the subject of some investigations[41,45,195]. Although, in the 2000-2500K region the rates for various third bodies do not differ by more than about a factor of two, at low temperatures the effects appear more pronounced. The available data are given in Table 1-1.1 and a plot of Log k vs. Pressure obtained in [195] is presented in Figure 1-1.6.

After evaluation of available data, Scholfield[28] found that if the rate of dissociation of N_2O is expressed in terms of a first order rate constant it varies with pressure according to an expression of the type:

$$k(\mathrm{sec}^{-1}) = A[M]/(1+B[M]) \qquad (1-1.4)$$

Figure 1–1.6. Logk vs Pressure



where A and B are constants. He suggested a simplistic scheme to illustrate such a general form:

$$N_2O + M \longleftrightarrow N_2O^* + M \qquad (1\text{-}1.5)$$

$$N_2O^* \longrightarrow N_2 + O \qquad (1\text{-}1.6)$$

$$N_2O + O \longrightarrow N_2 + O_2 \qquad (1\text{-}1.2)$$

$$N_2O + O \longrightarrow NO + NO \qquad (1\text{-}1.3)$$

More recently, Loirat et al.[46] studied the decomposition of N_2O in the pressure range 6.85-100 torr. They found that the activation energy shows a continued falloff with pressure with no indication of reaching a limit at the lowest pressure studied. This is in accord with the prediction of the theory of Lorquet, Lorquet and Forst (LLF)[47], and in considerable disagreement with the recommended values of Baulch et al.[10] The LLF theory reproduces, fairly well, the experimental concentration dependence of both the rate constants and activation energy. However, their experiments seem to indicate that activation energy may fall off with pressure somewhat faster than predicted by theory.

(2) N_2O Reactions with Ground State Oxygen Atoms and Molecules

Even though the values of the rate constants published for reaction (1-1.2) and (1-1.3) are widespread, the values of the ratio $k_{1-1.3}/k_{1-1.2}$ measured at the same temperature separate, essentially, into two groups, one with values of 0.9-1.2, and the other with values of 0.3-0.5[29,32,37,38,55,56] as can been seen in Figure 1-1.7. However, it seems to be generally agreed that this ratio is about unity as recommended by Baulch et al. in 1973[10].

The published rate data for reactions (1-1.2) and (1-1.3) and the published values for the branching ratio of the two reactions are given in Table 1-1.2 and 1-1.3 respectively and the Arrhenius plots of the rate constants for reactions (1-1.2) and (1-1.3) are given in Figure 1-1.8 and 1-1.9.

The values of $k_{1-1.2}$ and $k_{1-1.3}$ reported by several authors appear to have been estimated from measurements of N_2O decomposition. Hidaka et al.[57] calculated the concentration of NO produced in N_2O dissociation by using their values of $k_{1-1.2}$ and $k_{1-1.3}$ and those of Dean[44], which were about 20 times smaller than theirs, at a temperature ~1000K, and found almost no difference in the calculated results. Further they found that if the values for $k_{1-1.2}$ and $k_{1-1.3}$ were calculated from N_2O decomposition, they always obtained values smaller than actual. They also found that in the N_2O-H_2 system, the values calculated for $k_{1-1.2}$ and $k_{1-1.3}$ are sensitive

Figure 1–1.7. Branching Ratios

$N_2O + O(^3P) \dashrightarrow N_2 + O_2$ k1–1.2
$N_2O + O(^3P) \dashrightarrow NO + NO$ k1–1.3

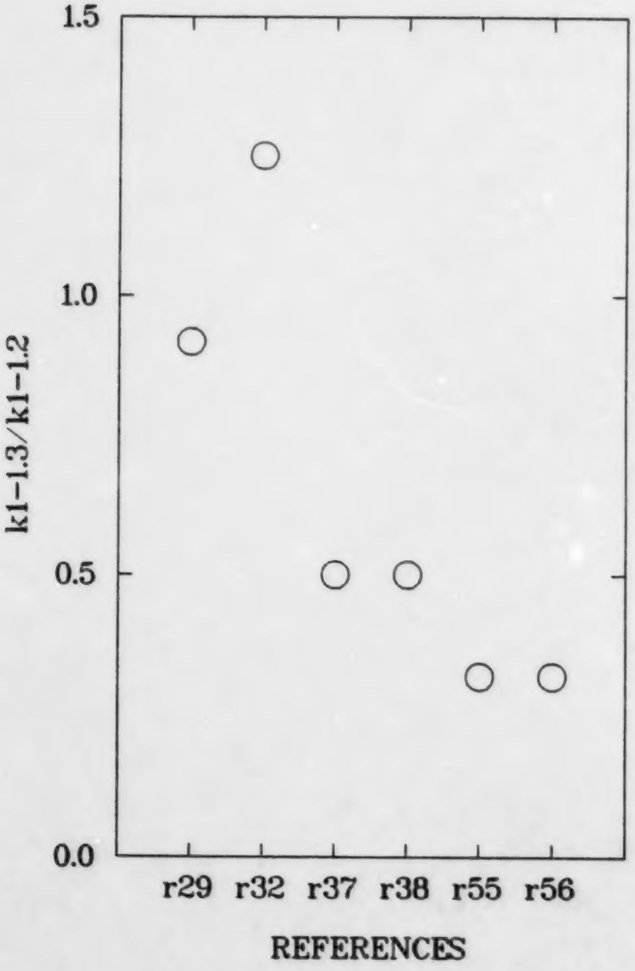


Figure 1–1.8a. N20 + 0 --> N2 + 02 (1)

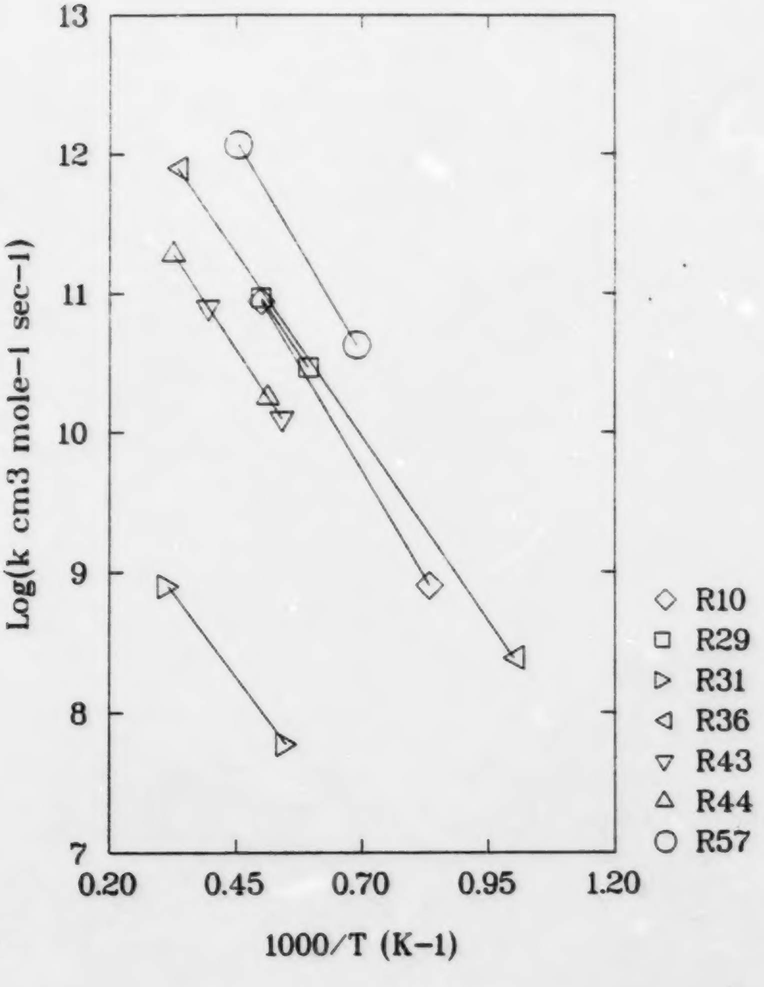


Figure 1-1.8b. N2O + O --> N2 + O2 (2)

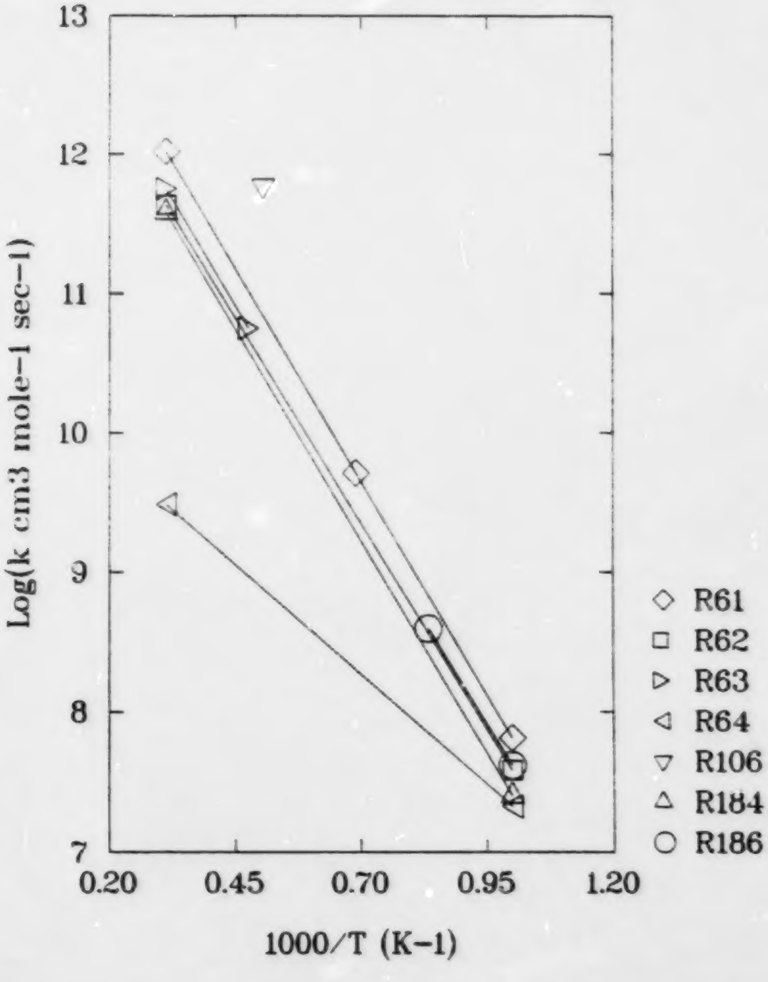
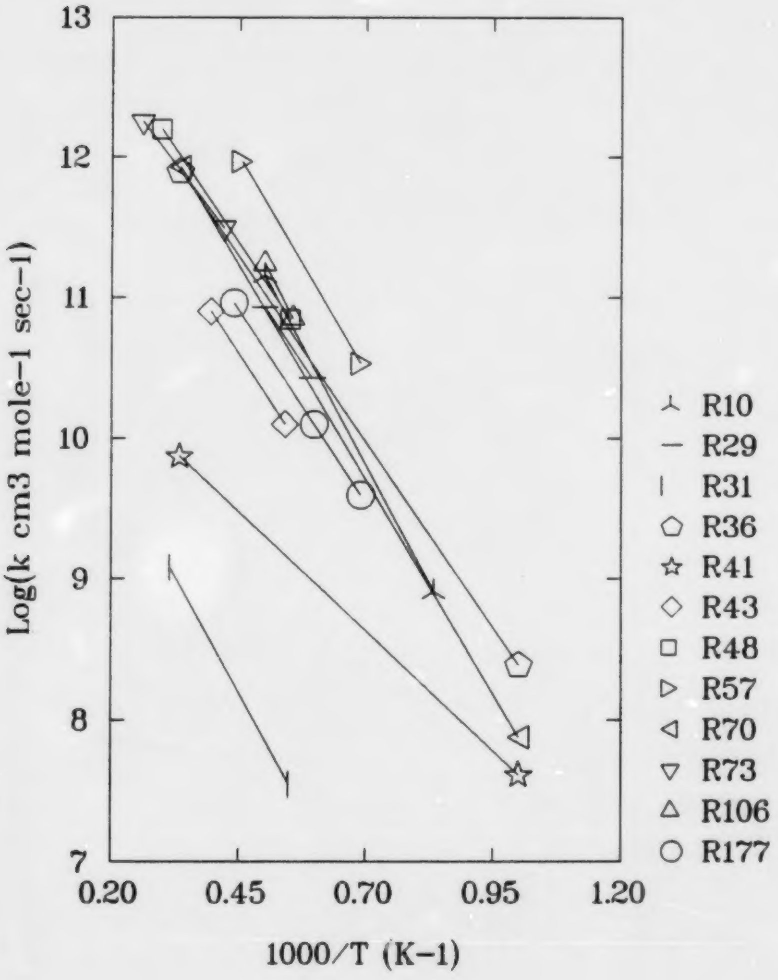


Figure 1–1.9. N2O + O --> NO + NO



to the final product concentrations. Consequently, they calculated $k_{1-1.2}$ and $k_{1-1.3}$ by fitting their experimental results to computer simulation of the N_2O-H_2 system based on a mechanism which included reactions (1-1.2) and (1-1.3). They then used the calculated values of $k_{1-1.2}$ and $k_{1-1.3}$ to interpret the results obtained in the N_2O decomposition.

There exists a third pathway for the reaction of N_2O with O-atoms, as shown in reaction (1-1.7).

$$N_2O + O \text{ --> } N + NO2 \qquad (1\text{-}1.7)$$

From rate data published in the 1960's[58-60], reaction (1-1.7) is too slow to have any significant effect on the destruction of N_2O at room temperature. However, there are no high temperature data available on the reaction (1-1.7) and its contribution in this region is unknown. If the rate constant $k_{1-1.7}$ is significant at high temperature, all results of $k_{1-1.1}$ based on only monitoring the decay of N_2O or production of NO must be suspect.

Published rate data for reaction (1-1.7) are also given in Table 1-1.2.

The reaction of N_2O with O_2 presents another possible channel for N_2O thermal destruction in excess O_2. In the early work of Ludwig[59], the rate constants for reactions (1-1.8) and (1-1.9),

$$N_2O + O_2 \dashrightarrow N + NO_3 \qquad (1\text{-}1.8)$$

$$N_2O + O_2 \dashrightarrow NO + NO_2 \qquad (1\text{-}1.9)$$

were reported as

$$k_{1\text{-}1.8} = 6.0\text{x}10^{14}(T)^{-1.5}\exp(-53239/T)\ \text{cm}^3\text{mole}^{-1}\text{sec}^{-1}$$

and

$$k_{1\text{-}1.9} = 6.0\text{x}10^{14}(T)^{-1.5}\exp(-9900/T)\ \text{cm}^3\text{mole}^{-1}\text{sec}^{-1}.$$

The value for $k_{1\text{-}1.8}$ differs significantly from the results given in [1] which were

$$k_{1\text{-}1.8} = 10^{13}\exp(-35000/T)\ \text{cm}^3\text{mole}^{-1}\text{sec}^{-1}.$$

The reported rate data for reactions (1-1.8) and (1-1.9) are also given in Table 1-1.2.

Table 1-1.2 Summary of Rate Parameters of Reactions with Oxygen Atoms and Molecules

BGAS	PRESSURE (torr)	TEMP(K)	E/R(K)	ERERR (%)	LOGA cm3/mole*s	AERROR %	N	LOGk cm3/mole*s	METHOD	DATATYPE	YEAR	REF
N2O + O --> N2 + O2												
			14090		13.929		0.0				1965	61
			13586		13.477		0.0				1964	62
			13999		13.477		0.0				1965	184
Ar		1000-3000	12128		13.653		0.0		ST,CHEMIL	FIT,RT	1972	36
		1200-2000	14090		14.000		0.0		CE	RECOM,	1973	10
Ar	456-2660	1450-2200	14090		14.845		0.0		ST,MS	FIT,EP	1985	57
Ar	1292-3496	1685-2000	12350	19.0	13.646	90.0	0.0		ST,V/UV E	FIT,RT	1979	29
Ar	186-435	1820-3170	11071		10.415		0.0		ST,V/UV E	FIT,RT	1980	31
Ar	60-74	1850-2535	12629		13.061		0.0		ST,V/UV E	FIT,RT	1975	43
Ar	37-77	1950-3075	12629		13.061		0.0		ST,IR	FIT,RT	1976	44
N2O	40	1980					0.0	11.771	FLAME,MS	FIT,EP	1977	106
		2100-3200	14090		13.660		0.0		ST		1977	63
		<6000	7296		10.477		0.0				1958	64
		Room	13501		13.477		0.0				1965	186
N2O + O --> NO + NO												
							0.0	8.778			1958	65
			16102	12.5	14.301		0.0				1958	66
			14090		14.000		0.0				1961	67
			14000		14.000		0.0				1963	68
							0.0	11.079			1963	60
			10567				0.0				1961	239
			16102		14.845		0.0				1962	69
			14090		13.079		0.0				1961	176
			14090		14.301	10.7	0.0				1962	39
			14000		13.954		0.0				1959	70
			12580	32.0	13.362	17.4	0.0				1966	71
			7800		11.000		0.0				1962	72
Ar		1000-3000	12128		13.653		0.0		ST,CHEMIL	FIT,RT	1972	36
		1200-2000	14090		14.000		0.0		CE	RECOM,	1973	10
Ar	456-2660	1450-2200	14090		14.748		0.0		ST,MS	FIT,EP	1985	57
		1673-2273	12580		13.361		0.0				1967	177
Ar	1292-3496	1685-2000	12350	19.0	13.610	80.0	0.0		ST,V/UV E	FIT,RT	1979	29
N2O	40	1800-2000	16103		14.732		0.0		FLAM,MS	AVMD,EP	1977	106
Ar	0-1	1815-3365	12349		13.794		0.0		ST,IR	FIT,RT	1977	48
Ar	186-435	1820-3170	15097		11.146		0.0		ST,V/UV A	FIT,RT	1980	31
Ar	60-74	1850-2535	12629		13.061		0.0		ST,V/UV	FIT,RT	1975	43
Ar	37-77	1975-3075	12629		13.061		0.0		ST,IR	FIT,RT	1976	44
		2384-3850	10970		13.490		0.0		ST		1979	73
		<6000	7800		11.000		0.0				1956	41
		Room	14000		14.079		0.0				1965	186
		Room	14090		14.000		0.0				1963	68
N2O + O --> N + NO2												
			25100		13.000		0.0				1963	58
			21034		14.568		-0.5				1961	59
			26670		12.000		0.0				1963	60
N2O + O --> Products												
Ar	2-75	2160-3400	12556	9.0	13.720		0.0		ST,LS	AVMD,RT	1975	74
N2O + O2 --> N + NO3												
			53239		14.778		-1.5				1961	59
			53238		14.778		-1.5				1961	59
N2O + O2 --> NO + NO2												
			9900		14.778		-1.5				1961	59
			35000		13.000		0.0				1966	175

Table 1-1.3. Branching Ratios of Reactions of
$N_2O + O(^3P)$ --> $NO + NO$ and
$N_2O + O(_3P)$ --> $N_2 + O_2$

TEMP.	BGAS	PRESSURE (Torr)	RATIOS	ERR%	METHOD	REF
1050-1200K	Ar	30-200	1.250	37.500	ST	32
1216-1655K	Ar	10-60	0.320	84.000	ST	55
1685-2560K	Ar	1292-3496	0.917	10.000	ST	29
1216-1655K	Kr	372	0.320	84.000	ST	56
1300-1950K	Kr	372	0.500	20.000	ST	38
1400-2000K	Kr	372	0.500	20.000	ST	37

(3) Photolysis of N_2O

Photolysis of N_2O over the wavelength region 185.0 - 230.0 nm yields electronically excited oxygen atoms[1,75]. Reaction (1-1.10) is the only primary process.

$$N_2O \text{ --> } N2 + O(^1D) \qquad (1\text{-}1.10)$$

Preston and Barr[1] investigated the possibility of the reaction

$$N_2O \text{ --> } NO + N(^4S) \qquad (1\text{-}1.11)$$

occurring in the photolysis of N_2O by adding a small amount of ^{15}NO. Photolysis at 219.3 nm and 228.8 nm showed that less than 1.7% $^{29}N_2$ formed by the reaction between N and NO indicating that the amount of N_2O which dissociated through reaction (1-1.11) was less than 2% of the amount of N_2O dissociated through reaction (1-1.10).

(4) N_2O Reactions with $O(^1D)$ Atoms

It is also generally accepted[1] that the subsequent steps following the primary step (1-1.10) are

$$N_2O + O(^1D) \rightarrow N_2 + O_2 \qquad (1\text{-}1.12)$$

$$N_2O + O(^1D) \rightarrow NO + NO \qquad (1\text{-}1.13)$$

Ogren et al.[76], Borisov et al.[77], and Amimoto et al.[16,78] determined that the deactivation process

$$N_2O + O(^1D) \rightarrow N_2O + O(^3P) \qquad (1\text{-}1.14)$$

is not important according to their measurements of

$$R = k_{1\text{-}1.14} \,/\, (k_{1\text{-}1.12} + k_{1\text{-}1.13})$$

which vary from $R = 0.04$ to $R = 0.12$.

Reaction (1-1.13) is believed to be the major source of NO in the natural stratosphere and therefore plays an important role in determining the ozone budget[79]. Estimations have been made of the effects of increased anthropogenic release of N_2O on stratospheric ozone, e.g., through the increased use of fertilizers and hydrocarbon combustion[79-82].

Most rate data for reactions (1-1.12) and (1-1.13) have been presented in the form of relative rates. Greenberg et al.[83] and Simonaitis[84] photolysed N_2O at 213.9 nm, and 184.9 nm, respectively, and using the method of chemical difference to determine the quantum yield of O_2, they calculated values for the branching ratio ($k_{1-1.12}$ / $k_{1-1.13}$) as 0.59±0.01 and 0.69±0.05, respectively. When Simonaitis added He to remove translational energy from the $O(^1D)$ atoms the ratio became 0.83±0.06[64]. Scott et al.[85] photolysed a mixture of NO_2 and N_2O at 242 nm and 229 nm and obtained a branching ratio of 1.01±0.06, while photolysis of mixtures of O_3 and N_2O at 250 nm and 229 nm yielded 0.99±0.06 and 1.08±0.19, respectively. Ghormley et al.[86] flash photolysed O_3 (>230nm) in a mixture of O_2 and N_2O and concluded that the branching ratio varies over a range of 0.83-1.01. It appeared that there were no wavelength effects on the ratio.

The branching ratios for reaction (1-1.12) and (1-1.13) are summarised in Table 1-1.4 and plotted in Figure 1-1.10, while the relative rate constants for overall reaction of N_2O with $O(^1D)$ atoms

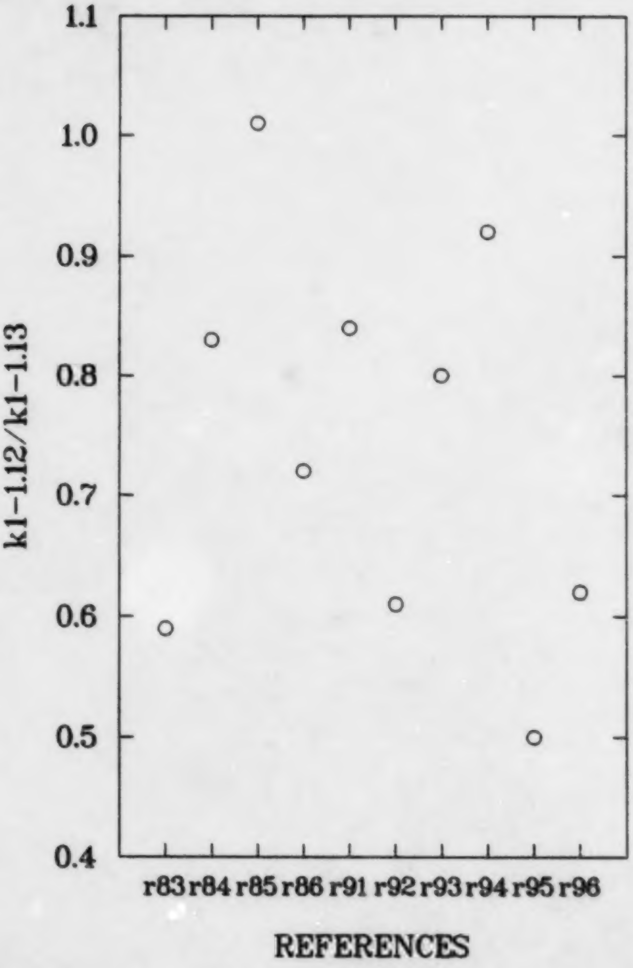
$$N_2O + O(^1D) \text{ --> Products} \qquad (1\text{-}1.15)$$

are summarized in Table 1-1.5.

There are few absolute rate data available for reactions (1-1.12) and (1-1.13) [16,87-89]. These data are given in Table 1-1.6.

Figure 1–1.10. Branching Ratios

N2O + O(1D) --> N2 + O2 k1–1.12
N2O + O(1D) --> NO + NO k1–1.13



However, one can conclude that the rate of reaction of N_2O with electronically excited oxygen atoms $O(^1D)$ at 298K seems about three orders of magnitude larger than that with ground state oxygen atoms at high temperature. Boxall et al.[90] studied the vibrational energy distribution among the products of the reaction (1-1.13) by flash photolysis of normal and isotopically labelled N_2O (^{15}NNO) and concluded that the total energy is divided equally between the two NO product molecules, with the major portion appearing as translational energy and that although the $O(^1D)$ atoms carry translational, as well as electronic excitation, their moderation by added Ar does not alter the observed vibrational energy distribution. It is suggested that reaction (1-1.13) occurs through an intermediate ONNO complex.

1-1.4 Branching Ratios of Reactions

$$\frac{N_2O + O(^1D) \dashrightarrow N_2 + O_2}{N_2O + O(^1D) \dashrightarrow NO + NO}$$

TEMP. (K)	Ratios	ERR%	METHOD	REF
	0.720		FP	86
	0.830	7.2	FP	84
	1.010	6.0	FP	85
172-436	0.846			91
177	0.610		FP	92
204-359	0.800		LP	93
290	0.920		FP	94
296	0.610		FP	92
298	0.500	20.0	FP	95
298	0.690	17.0	FP	84
298	0.590	20.0	FP	83
298	1.010	6.0	FP	85
300	0.800		FP	91
Room	0.620		FP	96

Table 1-1.5. Relative Rate of the Reaction
N2O + O(1D) --> Products

Reference Reactions	TEMP(K)	k/kr	ERROR (%)	METHOD	REF
O+RH->xROH+(1-x)(R.+OH)	298	0.145	10.0	FP	97
O(1D)+CF3Cl->Products	298	1.923		FP	87
O(1D)+O2->O(3P)+O2	298	5.000		FP	98
O(1D)+O2->O(3P)+O2	298	4.400		FP	99
O(1D)+O2->O(3P)+O2	298	3.600		FP	25
O(1D)+O3->2O2	298	0.390		FP	95
O(1D)+O3->2O2	298	0.250		FP	52
O(1D)+O3->2O2	298	0.670		FP	52
O(1D)+O3->Products	298	0.667		FP	100
N2O+O(1D)->O(3P)+N2O	295	0.120		LP	78
N2O+O(1D)->O(3P)+N2O	295	0.120			16
N2O+O(1D)->O(3P)+N2O	298	0.040		LP	76

Table 1-1.6. Rate constants of reaction of N2O with O(1D) atoms

REACTION	TEMP(T)	E/R(T)	LOGA	LOGk	METHOD	DATATYPE	YEAR	REF
			cm3/mole*s					
N2O+O(1D)->N2+O2	298K			14.080	FP		1975	100
N2O+O(1D)->N2+O2	298K			13.930	LP		1976	88
N2O+O(1D)->NO+NO	295K			13.860	LP	AVMD,RT	1981	16
N2O+O(1D)->NO+NO	297K			13.850	LP	AVMD,	1981	89
N2O+O(1D)->NO+NO	150-450K	0	13.640		CE	RECOM,	1984	17
N2O+O(1D)->NO+NO	100-300K	0	13.606			RECOM,	1987	11
N2O+O(1D)->N2+O2	298K			13.470		RECOM,	1987	11

1-2. REACTIONS OF N_2O WITH HYDROGEN ATOMS

The following reaction has been proposed as the primary step in the reaction of N_2O with hydrogen atoms.

$$N_2O + H \rightarrow OH + N_2 \qquad (1\text{-}2.1)$$

Current interest in the study of the reaction of N_2O with H-atoms is stimulated by the recognition that reaction (1-2.1) is one of the main chain propagating steps in the combustion of H_2/N_2O mixtures and N_2O supported hydrocarbon flames. It is , therefore, of direct importance in reaction mechanisms used for modelling the formation of NO from atmospheric nitrogen in combustion processes. For example, at $T<1800K$, the rate of NO formation will be determined by the competition between the reaction $O + N_2O \rightarrow 2NO$ and the reaction $H + N_2O \rightarrow N_2 + OH$ and regeneration of molecular nitrogen by unimolecular decomposition of N_2O[101]. In addition to its role in the modelling of NO formation in combustion system, reaction (1-2.1) could play a role as a reference reaction, since the formation of molecular nitrogen as a characteristic and stable product can be monitored.

Reaction (1-2.1) is well-known in thermal systems and has been studied at temperatures between 400 and 2600K in discharge-flow systems[101-104] by adding N_2O to slowly reacting mixtures of $H_2/O_2/He$ at 773K,[105] in flames,[106-109] and in shock tubes.[57,77,110-114] Most of the investigations derived values of $k_{1-2.1}$ by fitting experimental results to a complex mechanism using computer simulation. Thus, there is considerable uncertainty in individual rate coefficients. Only three direct measurements have been reported. Albers et al.[101] studied the reaction at temperatures from 720 to 1120K and pressures of 2.6 to 8.0 torr and gave a value of

$$k_{1-2.1} = (2.2\pm0.7)\mathrm{x}10^{14}\exp(-8708/T)\ \mathrm{cm^3mole^{-1}sec^{-1}}.$$

Marshall and Fontijn[33] extended the pressure and temperature ranges so as to be closer to those relevant to practical combustion and provided a rate constant of

$$k_{1-2.1} = 3.3\mathrm{x}10^{10}\exp(-2380/T)+4.4\mathrm{x}10^{14}\exp(-9690/T)\mathrm{cm^3mole^{-1}sec^{-1}}.$$

Dean and Steiner[114] also reported a value of the rate constant for reaction (1-2.1) as

$$k_{1-2.1} = 10^{15.258}\ \exp(-13591/T)\ \mathrm{cm^3mole^{-1}sec^{-1}}.$$

The published rate data for reaction (1-2.1) are summarized in Table 1-2.1 and the Arrhenius plots of the rate constants for reaction (1-2.1) are given in Figure 1-2.1.

Table 1-2.1 Summary of Rate Parameters of Reactions of N20 with Hydrogen

BGAS	PRESSURE (torr)	TEMP(K)	E/R(K)	ERERR (%)	LOGA cm3/mole*s	AERROR %	N	LOGk cm3/mole*s	METHOD	DATATYPE	YEAR	REF
N20 + H --> OH + N2												
			8202	12.0	14.623						1959	108
			8051		14.602						1959	70
			8051		14.477						1964	45
			6542		13.700						1965	109
		298						9.540	FP		1973	115
		423-1760	6542		13.700						1965	109
		423						7.000			1962	102
	500	460-2500	7599	7.0	13.881						1973	105
		600						10.633			1965	76
		700-2500	7598		13.880				CE	RECOM	1973	10
He	3-9	718-1111	8708	4.0	14.342	31.8			FT,V/UV A	FIT,RT	1975	101
He	500	773						9.415	S/LF,GC	RELAT,EP	1973	105
		773						9.420	T		1973	105
H2		773						9.415	S/LF	RELAT,EP	1973	116
		900						10.630	FLAME		1965	109
		900						10.630	FLAME		1965	107
N20	40	1000-1700	6592		13.778	33.0			FLAME,MS	FIT,EP	1977	106
		1263-1783	8202		14.020				FLAME		1959	108
		1357						11.462			1965	107
		1357						11.460	FLAME		1965	107
Ar	456-2660	1450-2200	7548		14.176				ST,MS	FIT,EP	1985	57
Ar	5-20	1473-2710	8505	4.0	13.583	16.9			FT,CHEMIL	FIT,RT	1979	104
		1473-2710	8500		13.580				FD	FIT,	1979	104
Ar	380-760	1475-2875	8152	40.0	13.515	14.0			ST,IR	FIT,RT	1979	110
Ar	1870-2348	1695						12.146	ST,V/UV A	RELAT,RT	1980	111
Ar	126-175	1700-2500	11065		14.956				ST,IR	FIT,RT	1980	112
		1700-2600	6038		13.400				ST		1969	113
Ar	135-178	2000-2850	13591		15.258				ST,V/UV A	AVMD,RT	1978	114
He	2.6-8.0	720-1120	8708		14.342	30.0			FT,ESR	AVMD,RT	1975	101
Ar	80-430	385-1314	See Text						HTP	AVMD,RT	1987	33
N20 + H --> NH > NO												
			15096		11.000	0.5			ESTIM,		1965	175
Ar	760-9120	850-2000	14594	5.0	14.800				ST,V/UV A	FIT,RT	1978	77
Ne		873						7.720			1975	117
		950-2500	14600		14.800				ST		1978	77

Based on the large rate constant observed for reaction (1-2.1) it is reasonable to suggest that there will be no net increase in the concentration of N_2O within flame zones since N_2O would be removed rapidly by reaction (1-2.1).

A second pathway is available for the reaction of H with N_2O, as shown in reaction (1-2.2),

$$N_2O + H \text{ --> } NO + NH \qquad (1\text{-}2.2)$$

Figure 1–2.1a. N2O + H --> OH + N2 (1)

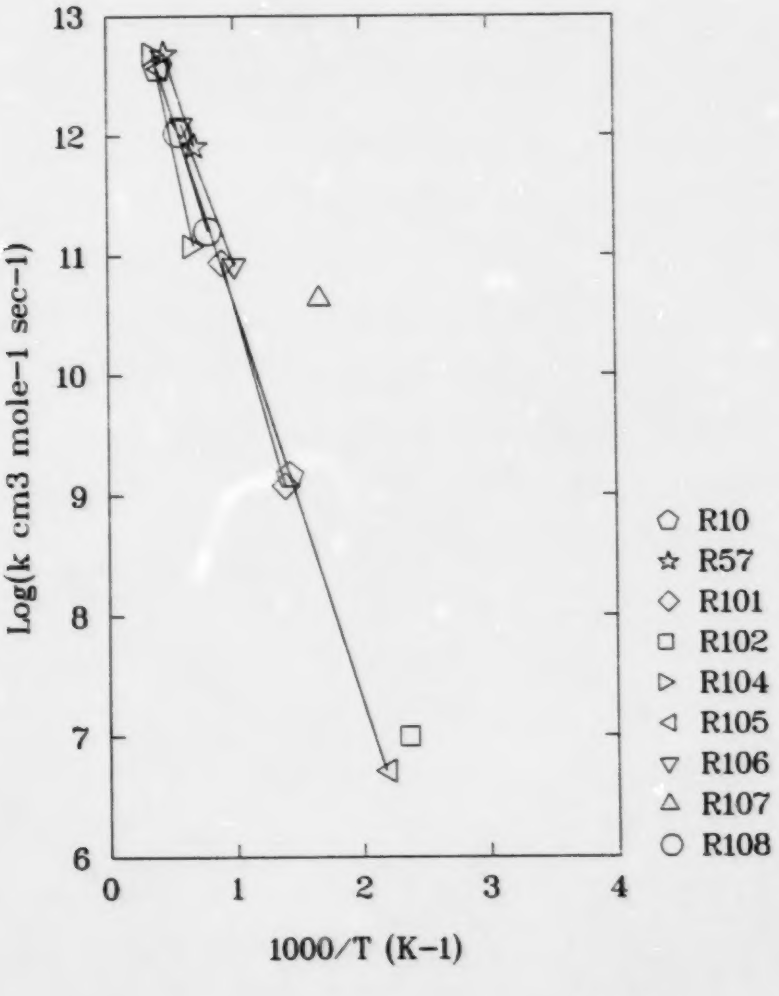
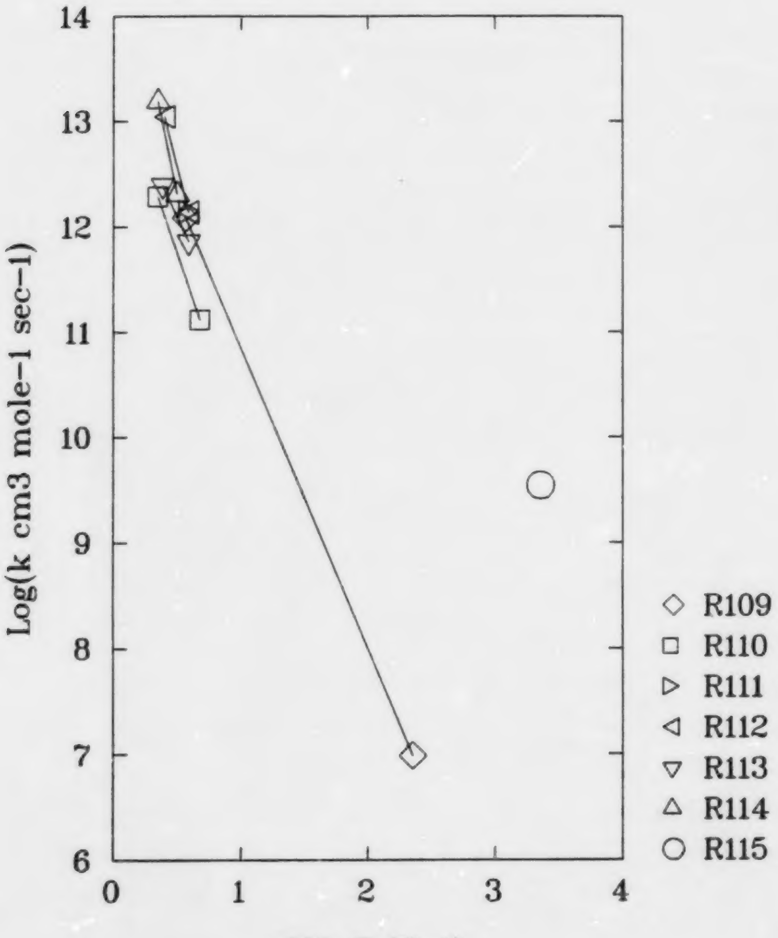


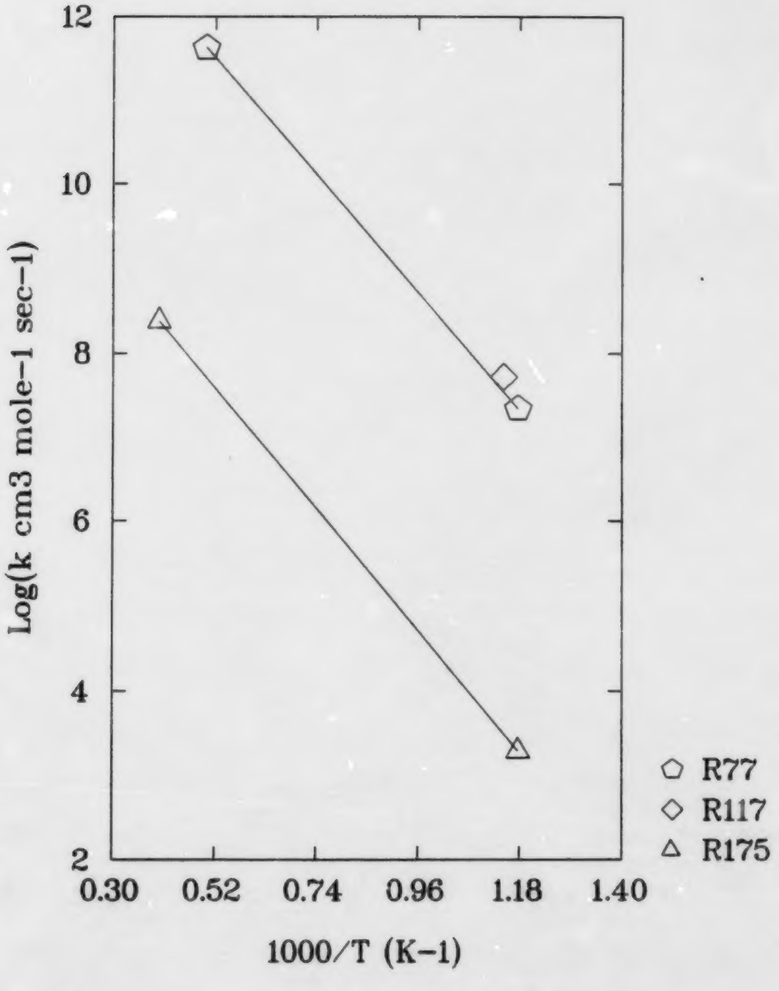
Figure 1–2.1b. N2O + H --> OH + N2 (2)



However, reaction (1-2.2) has been reported only as a minor process in high-temperature nitrous oxide-hydrogen flames[109]. Only four reports of studies of this reaction have been located and their results are also included in Table 1-2.1 and the Arrhenius plots for this reaction are given in Figure 1-2.2. These reports all indicate a sizeable activation energy for reaction (1-2.2).

In 1969, Oldershaw and Porter[118] showed that both reactions (1-2.1) and (1-2.2) occur if the hydrogen atoms are generated by photolysis of HI. In keeping with the high threshold energy for reaction (1-2.2), reaction (1-2.1) was predominant at all wavelengths used while (1-2.2) was observed only at the shortest wavelengths, presumably as a result of the involvement of hot hydrogen atoms. The occurrence of reaction (1-2.2) has been confirmed by the observation of ammonium iodide in flashed mixtures of HI and N_2O[119]. In 1972, Oldershaw and Porter[120] published a further investigation on the reaction of hot H atoms with N_2O in which they determined net probabilities of reactions (1-2.1) and (1-2.2) as a function of the initial kinetic energy of H atoms by analysis of the products of photolysis, at various wavelengths. The results have been used to calculate a crude excitation function for reaction (1-2.1) which provided a correlation of the photolysis and thermal experiments. Their results showed that hot atom results were consistent with measurements of the rate of (1-2.1) in thermal systems at high temperatures.

Figure 1-2.2. $N_2O + H \rightarrow NH + NO$



1-3. REACTIONS OF N_2O WITH CO AND NO

(1). Reaction with CO

It has been generally accepted that the reaction of CO with N_2O proceeds via two channels; (i) a highly exothermic bimolecular reaction (1-3.1), which plays an important role below 2000K,

$$N_2O + CO \dashrightarrow CO_2 + N_2 \qquad (1\text{-}3.1)$$

and (ii) a set of reactions initiated by the dissociation of N_2O[121].

To the present, some studies devoted to the investigation of the reaction of N_2O with CO have been published [55,56,121-128].

Bawn[124] studied the reaction near 820K in a static system. However, due to the presence of simultaneous chain reactions and heterogeneous complications, he could not evaluate the rate constant for reaction (1-3.1). Lin and Baner[125] studied the reaction (1-3.1) in N_2O and CO mixtures, highly diluted with Ar, in a single-pulse shock tube in the temperature range 1320-2280K. They reported that the direct bimolecular reaction occurs in the temperature range of their study and that this reaction was dominant below approximately 1500K. Due to a lack of knowledge of the relative contributions of various elementary steps to the observed rate of reaction, they developed a numerical computation technique and obtained an estimation for the rate constant of reaction (1-3.1). Since their work, several shock tube investigations have been published extending the temperature range from 1060-2500K[55,56,121]. However, there are large discrepancies among those reported rate constants as shown in Table 1-3.1 and Figure 1-3.1.

Table 1-3.1. Summary of Rate Parameters of the Reaction
N2O + CO --> CO2 + N2

BGAS	PRESSURE (torr)	TEMP(K)	E/R(K)	ERERR%	LOGA cm3/mole*s	METHOD	DATATYPE	YEAR	REF
CO	1-300	1060-1220	22142	7.0	13.700	S/LF,CHEMIL	FIT,EP	1983	121
Ar	15	1076-1228	23147	4.0	14.400	S/LF	FIT,RT	1987	46
Kr	372	1169-1655	8706	13.0	11.320	ST,GC	AVMD,RT/EP	1973	56
Ar	10-60	1169-1655	10568	10.0	11.850	ST,GC	AVMD,RT/EP	1976	55
He	1900	1350-2100	10223		11.505	ST,IR	FIT,RT	1985	122
Ar		1430-1910	11575		11.041	ST,	FIT,	1969	125
CO	70-300	1500-1900	26671	8.0	14.850	ST,CHEMIL	AVMD,RT	1979	123
Ar	70-300	1700-2500	25161	2.0	15.439	ST,CHEMIL	AVMD,RT	1979	123

Zaslonko et al.[123] proposed an activation model of the exchange reaction (1-3.1) as follows,

$$N_2O + M \dashrightarrow N_2O^* + M \qquad (1\text{-}3.2)$$

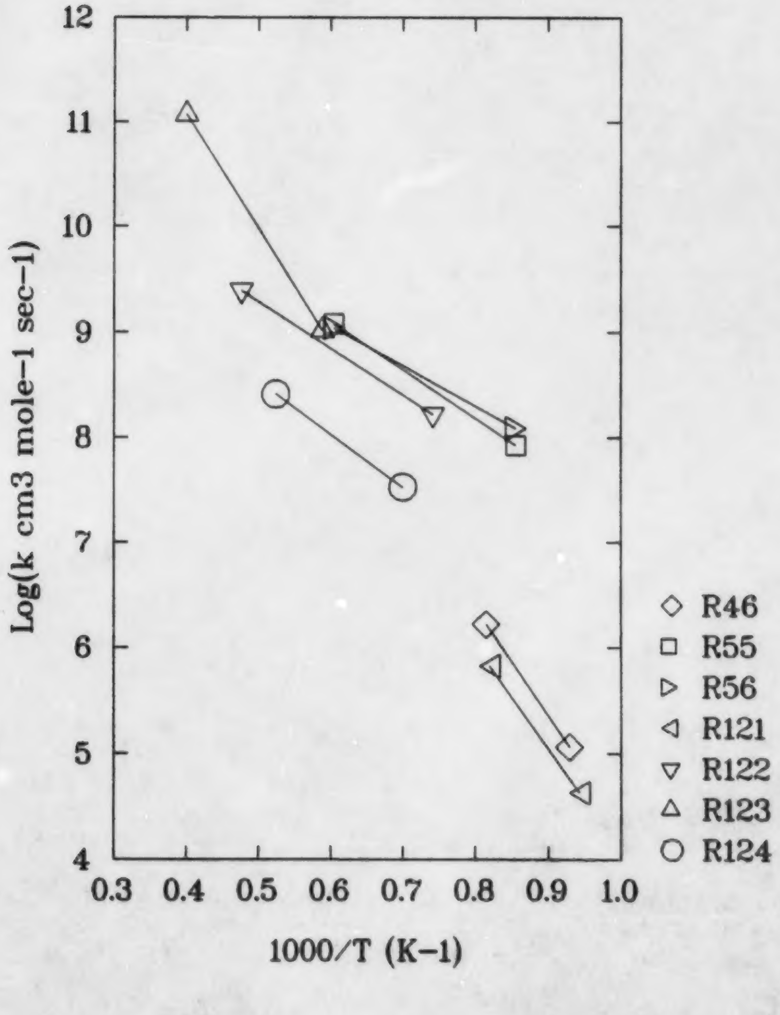
$$N_2O^* + CO \dashrightarrow (N_2O^*CO)^\# \qquad (1\text{-}3.3)$$

$$(N_2O^*CO)^\# + M \dashrightarrow N_2O + CO + M \qquad (1\text{-}3.4)$$

$$(N_2O^*CO)^\# \dashrightarrow N_2 + CO_2 \qquad (1\text{-}3.5)$$

Here N_2O^* represents activated molecules and $(N_2O^*CO)^\#$ is an intermediate transition state. From a comparison of the proposed model with experiment, they obtained the rate constant for

Figure 1–3.1. N2O + CO --> CO2 + N2



activation of N_2O to N_2O^* as

$$k_{1\text{-}3.2}(M{=}Ar) = 1.97\times10^{8}\ cm^{3}mole^{-1}sec^{-1},$$

and found the rate constant for the reaction of highly excited N_2O^* with CO, $k_{1\text{-}3.3}$, to be about equal to that for binary collisions (1-3.1).

Recently, the possibility that the CO/N_2O system might play a role in CO_2 gas-dynamic lasers[126-128] stimulated the investigation of the rate of reaction (1-3.1). Fujii et al.[122] studied reaction (1-3.1) by comparison of calculated infrared emission profiles of CO_2 with those observed in shock-tube experiments in the temperature range 1350-2100K. They reported the rate constant for reaction (1-3.1) as

$$k_{1\text{-}3.1} = 3.2\times10^{11}\exp(-10223/T)\ cm^{3}mole^{-1}sec^{-1}$$

Recently, Loirat et al.[46], using a static reactor, obtained the rate constant for direct reaction of CO with N_2O over the temperature range 1076-1228K at a pressure of 15 torr. They found that under these conditions, the reaction proceeds essentially according to the direct reaction (1-3.1). The Arrhenius expression derived from their experiments is

$$k_{1\text{-}3.1} = 10^{14.4\pm0.3}\exp[-(23147\pm1006/T]\ cm^{3}mole^{-1}sec^{-1}$$

They suggested that the uncertainties in side reactions do not greatly influence the value of $k_{1-3.1}$. In spite of remaining uncertainties in the reaction mechanism, this result, obtained at low temperature suggests that the low activation energies reported for reaction (1-3.1) by several authors[55,56,122,125] from experiments performed at higher temperature, are highly suspect.

(2) Reaction with NO

The reaction of N_2O with NO, i.e.,

$$N_2O + NO \rightarrow NO_2 + N_2 \qquad (1\text{-}3.6)$$

has been studied in less detail than the reactions of N_2O with oxygen atoms. However, under certain conditions this reaction can appreciably influence the destruction of N_2O and change the composition of the final products[129]. Hinshelwood and Mucgrare[130] noted, for the first time, that addition of NO increases the rate of N_2O thermal destruction. A calculation of the rate constant of reaction (1-3.6) from experimental data led the authors to the value

$$k_{1-3.6} = 3\times10^{16}\exp(-31450/T)\ \mathrm{cm^3mole^{-1}sec^{-1}}$$

with anomalously high values for the activation energy and the pre-exponential factor. Kaufman and Kelso[131] have shown reaction (1-

3.6) is first order in N_2O and NO and calculated a bimolecular rate constant of

$$k_{1\text{-}3.6} = 2.5\text{x}10^{14}\exp(-25610/T)\ \text{cm}^3\text{mole}^{-1}\text{sec}^{-1}$$

over the temperature range 1700-2500K. Fishburne and Edse[22] established that, when there is excess NO, the decomposition of N_2O in the range 1700-2200K, proceeds at a rate which exceeds the rate of decomposition of N_2O in Ar by approximately twofold. The value of $k_{1\text{-}3.6}$ obtained by Fishburne and Edse[22] coincides with the value obtained by Kaufman and Kelso[131], but differs considerably from the results of Hinshelwood and Mucgrare[130].

Borisov et al.[129] refined the kinetic parameters of reaction (1-3.6) over a wide temperature range in static overflow and shock tube experiments. They measured so called ignition lags, t_{il}, defined in the static overflow set-up as the time from completion of overflow of the gas mixture into a reaction vessel (which had been pumped out and heated to a known temperature) to the beginning of the sharp increase in the pressure upon explosion, and in the shock tube as the time from the moment of arrival of the reflected shock wave at the end of the tube to the start of the rapid decrease in N_2O concentration. They then compared the experimentally measured ignition lags with the lags calculated theoretically by a joint analytical solution of the kinetic equations for the reaction system.

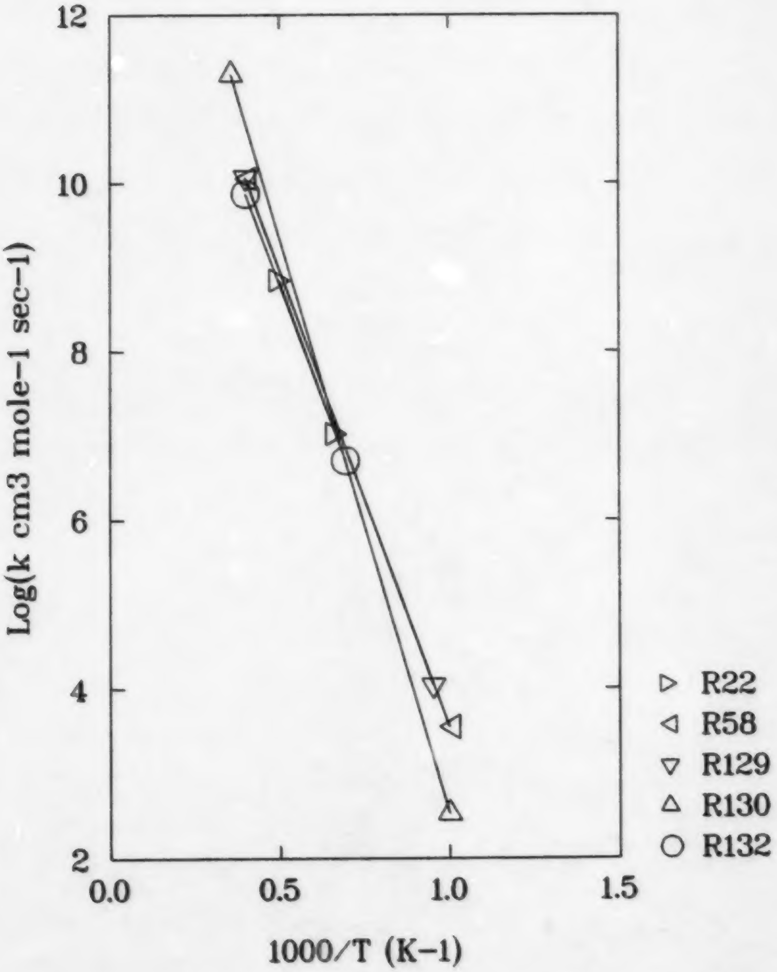
In 1979, Gvozdev et al.[132] studied N_2O reaction kinetics in mixtures of NO_2, NO and O at 713-950K. They found that at these relatively low temperatures, the reaction of N_2O with NO proceeds by the same mechanism and with same kinetic parameters as over the extended temperature range 713-2500K.

There have been no recent publications describing work on reaction (1-3.6). A summary of the rate parameters for reaction (1-3.6) is given in Table 1-3.2 and the Arrhenius plots of the rate constants for reaction (1-3.6) are presented in Figure 1-3.2.

Table 1-3.2. Summary of Rate Parameters of the Reaction of N2O + NO -->NO2 + N2

BGAS	PRESSURE (torr)	TEMP(K)	E/R(K)	ERR %	LOGA cm3/mole* s	METHOD	DATATYPE	YEAR	REF
			25160		14.398			1958	64
			25160		14.398			1963	58
			25160		14.398			1955	131
			25000		14.398			1963	58
Ar	304-760	1050-2500	25161	6.0	14.439	ST,V/UV A	FIT,RT	1973	129
		1500-2000	25160		14.300	ST		1964	22
N20	23-113	1440-2500	24809	1.0	14.179	S/LF	FIT,RT	1979	132
			31450		16.177			1932	130

Figure 1–3.2. N2O + NO ––> NO2 + N2



1-4. REACTIONS OF N_2O WITH MISCELLANEOUS MOLECULES

(1) Reaction with OH

Interest in the reaction of OH with N_2O was stimulated by the search for a tropospheric chemical sink for N_2O [133-136]. Johnston and Selwyn[133] have calculated the stratospheric residence time of N_2O to be 170 years based on their measurements of the N_2O absorption spectrum and on its removal by stratospheric reactions such as with $O(^1D)$. This residence time is much longer than the estimate of about 12 years by Schutz et al.[134], Junge and Hahn[135], and Hahn[136] which were inferred from the strength of the oceanic sources of nitrous oxide. From this discrepancy it has been concluded that there exists a major tropospheric sink for N_2O. Johnston and Selwyn[133] have stated that if this sink is a homogeneous gas phase reaction of N_2O with a species X, with a rate constant k, then k[X] is about $3X10^{-9}s^{-1}$. For OH to be considered as X, an overall rate constant of approximately $6.02x10^8$ $cm^3mole^{-1}sec^{-1}$ would be necessary for the reaction of N_2O with OH, since the tropospheric concentration of OH is approximately $3x10^6$ molecule cm^{-3}.

An upper limit for the rate constant of reaction (1-4.1)

$$N_2O + OH \dashrightarrow HO_2 + N_2 \qquad (1-4.1)$$

has been determined by Gordon and Mulac[137] to be

$$k_{1-4.1} < 1.204\times10^{10}\ \mathrm{cm^3mole^{-1}sec^{-1}}$$

at 440K which does not necessarily exclude reaction (1-4.1) as a major atmospheric sink of N_2O.

Later, Biermann et al.[138] determined the rate constant of reaction (1-4.1) to be

$$k_{1-4.1} = (2.29\pm0.72)\times10^{7}\ \mathrm{cm^3mole^{-1}sec^{-1}}$$

at 298K by resonance fluorescence. This value would definitely exclude reaction (1-4.1) as a major atmospheric removal process for N_2O. The values obtained by Chang[139] and Atkinson et al.[140] agree with that of Biermann et al. at 298K and are two orders of magnitude smaller than that of Gordon et al.[137].

A summary of available rate data on the reaction N_2O with OH are given in Table 1-4.1.

(2) Reaction with HO_2

Hydroperoxyl radicals (HO_2) have long been recognized as playing an important role in hydrocarbon oxidation processes at combustion temperatures,[141,142] and in the chemistry of the troposphere and stratosphere[143,144].

Only two studies of the reaction of HO_2 with N_2O have been published. They each present an upper limit for the rate constant obtained by a competitive method [145,146]. The values reported have a discrepancy of almost three orders of magnitude at 300K. Ignoring the discrepancy, both values at this low temperature indicate that the reaction of N_2O with HO_2 need not be considered as a possible N_2O sink in troposphere. No high temperature data have been reported for this reaction.

The values published are presented in Table 1-4.1.

(3) Reaction with CH

Reactions of CH are important sources of ionization and luminescence in hydrocarbon combustion and are thought to serve as intermediaries in both the formation and removal of nitrogen oxides. Two investigations on the reaction of CH with N_2O have been published[147,148].

Wagal et al.[147] produced CH radicals by infrared multiphoton dissociation of CH_3NH_2, CH_3CN, and cyclo-C_3H_6 using a pulsed CO_2 laser. The subsequent removal of CH by reaction with N_2O was observed by laser induced fluorescence. The rate constant of the overall reaction (1-4.2)

$$N_2O + CH \text{ --> Products} \qquad (1\text{-}4.2)$$

was determined as

$$k_{1-4.2} = 4.7\text{x}10^{13}\ \text{cm}^3\text{mole}^{-1}\text{sec}^{-1}$$

at 298K.

Anderson et al.[148] studied the reaction (1-4.2) in a flow tube, and their value of the rate constant of reaction (1-4.2) is

$$k_{1-4.2} = 2.53 \times 10^{13}\ \ \text{cm}^3\text{mole}^{-1}\text{sec}^{-1}$$

at 298K.

These results indicate that CH radicals should play an important role in removal of N_2O in atmospheric and combustion processes.

The reaction paths which are energetically available include the following,[147]

$$N_2O + CH \text{ --> } N_2 + HCO \qquad (1\text{-}4.2a)$$

$$N_2O + CH \text{ --> } CO + N_2 + H \qquad (1\text{-}4.2b)$$

$$N_2O + CH \text{ --> } NO + HCN \qquad (1\text{-}4.2c)$$

$$N_2O + CH \text{ --> } N + HNCO \qquad (1\text{-}4.2d)$$

$N_2O + CH \text{ --> } NH + NCO$ (1-4.2e)

$N_2O + CH \text{ --> } OH + NCN$ (1-4.2f)

$N_2O + CH \text{ --> } CN + HNO$ (1-4.2g)

The reactions (1-4.2a) and (1-4.2c) involve the making and breaking of only one bond and are spin allowed. Up to the present, no investigation of the branching ratio of these reactions has been reported, even though it seems important to study the formation of HCO and HCN which might play an important role in N_2O formation.

A summary of the published rate parameters for reactions of N_2O with miscellaneous molecules is given in Table 1-4.1.

Table 1-4.1 Summary of Rate Parameters of the Reactions of N2O with Miscellaneous Molecules

REACTION	BGAS	PRESSURE (torr)	TEMP(K)	E/R(K)	LOGA	LOGk	KERROR	METHOD	DATATYPE	YEAR	REF
					cm3/mole*s						
N2O+OH->HO2+N2	He	2-4	298-480	2899	11.004			FT,RF	ULMD,RT	1978	139
	Ar	50	298			7.359	31.878	FT,V/UV A	AVMD,RT	1976	138
	N2	2-4	298-480			8.382		FT,RF	ULMD,RT	1977	149
N2O+OH->Products	Ar	25-654	298-443			8.082		S/LF,,RF	ULMD,RT	1976	140
	H2O	10-760	440			10.000		S/LF,V/UV A	ULMD,RT	1975	137
N2O+HO2->Products	N2	760	300			4.083		S/LF,FTIR	RELAT,RT	1979	145
	He	1	300			6.381		FT,LMR	RELAT,RT	1979	146
N2O+CH->Products	Ar	5	298			13.672	18.000	S/LF/P,LIF	AVMD,RT	1982	147
	He		298			13.403		FT,RF	AVMD,RT	1987	148
N2O+CH3->CH3O+N2	Ar	760	1000-2000	14276	15.000			ST	ULMD,RT	1977	150
	CH4	2-170	873			7.146	20.714	S/LF,GC	RELAT,EP	1973	152
N2O+CH3O->Products	SF6	5	298			10.000		S/LF/P,LIF	ULMD,RT	1980	155

(4) Reaction with CH_3

Nitrous oxide is a convenient source of oxygen for the determination of kinetic parameters for CH_4 oxidation and for studies of the oxidative cracking of CH_4. The reaction between CH_3 and N_2O may also be of interest, as one of the possible destruction paths of nitrous oxide in combustion.

The high temperature oxidation of methane by nitrous oxide has been studied by several authors[150-154]. The final reaction products have been identified [150,153] as nitrogen, ethane, carbon monoxide, and water. A mechanism which included the thermolysis of N_2O i.e., reactions (1-1.1)-(1-1.3) was suggested on the basis of a material balance of the process.

In the presence of methane, the reaction of CH_4 with O atoms,

$$O + CH_4 \dashrightarrow OH + CH_3 \qquad (1\text{-}4.3)$$

competes with reactions (1-1.2) and (1-1.3). Only about 0.1% of the O atoms react with N_2O[152]. The following reactions (1-4.4) and (1-4.5) must also be included in the mechanism to account for the major products water and ethane.

$$OH + CH_4 \text{ --> } H_2O + CH_3 \qquad (1\text{-}4.4)$$

$$2CH_3 \text{ --> } C_2H_6 \qquad (1\text{-}4.5)$$

The observed value of between 1 and 2 for the ratio $[N_2]$/[C containing compounds] in the products suggested that further reactions of N_2O occur in the system as follows,

$N_2O + CH_3 \rightarrow N_2 + CH_3O$ (1-4.6)

$CH_3O \rightarrow H + CH_2O$ (1-4.7)

$H + CH_4 \rightarrow H_2 + CH_3$ (1-4.8)

$H + N_2O \rightarrow OH + N_2$ (1-2.1)

Reactions (1-4.6 to 1-4.8) comprise one chain mechanism while reactions (1-4.6),(1-4.7),(1-2.1), and (1-4.4) comprise an alternative chain mechanism, with reaction (1-4.5) as the chain termination step[152] in each case.

Fitting their experimental data to this mechanism, Falconer et al.[152] derived a rate constant of

$$k_{1-4.6} = (1.4 \pm 0.3) \times 10^{7}\ cm^{3} mole^{-1} sec^{-1}$$

at 873K for reaction (1-4.6).

The combustion of CH_4-N_2O-Ar mixtures was studied by Drummond [151] at 1500<T<2000K and Soloukhin[154] at 2000K<T<2700K using a shock tube method. The effective parameters and expressions for the temperature dependence of the combustion lag obtained by Drummond and Soloukhin differ considerably, thereby leading to various interpretations of the experimental data. Since the activation energy of the reaction of CH_4 with N_2O reported by Drummond[151] is close to that for N_2O decomposition, it is reasonable to assume that the reaction kinetics are controlled by the rate of N_2O

decomposition. The effective activation energy of this reaction, as determined by Soloukhin,[154] was 30 kcal/mole, which led the author to suggest a branched-chain reaction mechanism.

Borisov et al.[150] studied the combustion of CH_4-N_2O-Ar mixtures in a shock tube at 1000-2000K. An analytical expression for the adiabatic combustion lag has been obtained in a quasi-stationary approximation. The comparison of calculated lag values with experimental data obtained for CH_4-N_2O-Ar and N_2O-Ar mixtures has shown that the combustion of CH_4-N_2O-Ar mixtures in the temperature range 1000-2000K is thermal in nature and that the reaction kinetics are determined by the rate of N_2O decomposition. The upper limit of the rate constant for reaction (1-4.6) has been given as[150]

$$k_{1\text{-}4.6} < 10^{15}\exp(-14276/T)\ \text{cm}^3\text{mole}^{-1}\text{sec}^{-1}$$

over a temperature range 1000-2000K.

The rate data for the reaction (1-4.6) are also listed in Table 1-4.1.

(5) Reaction with CH_3O

Only one upper limit value of the rate constant has been reported for the reaction of CH_3O with N_2O.[155]

$N_2O + CH_3O \text{ --> Products}$ (1-4.9)

In this work, CH_3O was produced by the 266nm photolysis of CH_3ONO and monitored by laser induced fluorescence. The reaction of CH_3O with N_2O was too slow to measure under the experimental conditions used, and only an upper limit was calculated as:

$$k_{1-4.9} < 1.2x10^{10} \ cm^3 mole^{-1} sec^{-1}$$

at 298K.

1-5. REACTIONS OF N_2O WITH MISCELLANEOUS ATOMS

There are many reports of studies of reactions of N_2O with atoms. Husain et al. investigated the reaction of N_2O with C[156,157], Si[158], P[159], and Sn[160] atoms by resonance absorption and obtained the rate constants for these reactions at 300K. Kashireninov et al.[161] studied the reaction of N_2O with Mg, Ca, Sr, and Ba atoms over the temperature range 823-1073K and obtained Arrhenius parameters for the reactions. Kaufman and Gerri[162] studied the reaction of N_2O with the halogen atoms, Cl Br, and I, and obtained Arrhenius parameters over the temperature range 876-1031K.

During the 1970's, attempts to develop a visible light chemical laser generated interest in the reactions of Group IV atoms with N_2O[163-165]. Wiesenfeld and Yuen[165] and Felder and Fontijn[163] studied the reactions of N_2O with Sn atoms by using flash photolysis / time resolved atomic absorption and high temperature fast-flow reactor studies over the temperature range 530-950K. The rate constants obtained by the three authors agree reasonably well, but the activation energies obtained differed considerably as follows; $E/R=1876K$[160] ,2013K[165], and 3000K[163].

More recently, Piper et al.[166] reported the rate constant for the reaction of N_2O with $N(^2D)$ at 300K, and Plane and Rajasekhar[167] reported the Arrhenius parameters for reaction of N_2O with Na atoms at 280-850K.

Several authors have studied the dynamics of the reactions of N_2O with Ba[168,169] and Al[170] using a molecular beam method.

A summary of the rate parameters of reactions of N_2O with miscellaneous atoms is given in Table 1-5.1 and the Arrhenius plots of the rate constants for reactions of N_2O with Sn atoms and halogen atoms are presented in Figure 1-5.1 and 1-5.2, respectively.

Table 1-5.1. Summary of Rate Parameters of the Reactions of N2O with Miscellaneous Atoms

REACTION	TEMP(K)	E/R(K)	ERERR%	LOGA	LOGk cm3/mole*s	KERROR%	METHOD	DATATYPE	YEAR	REF
N2O+Ba->Products	923-1073	2818		13.180					1977	161
N2O+C->Products	300				13.179	63.5	LF/FP,V/UV A	AVMD,RT	1971	156
	300				12.894	23.0	LF/FP,V/UV A	AVMD,RT	1975	157
N2O+Ca->Products	923-1073	2818		13.200					1977	161
N2O+Ge->GeO+N2	300				11.610				1977	164
N2O+Mg->Products	823-1073	3321		13.110					1977	161
N2O+Na->Products	280-850	1590	3.0	14.230			FP,LIF	AVMD,RT	1989	167
N2O+N(2D)->Products	300				12.114	14.0	RF	AVMD,RT	1987	166
N2O+P->Products	Room				9.480			ULMD	1977	159
N2O+Si->Products	300				14.060				1978	158
N2O+Sn->Products	298-670	1876		11.420					1978	160
	341-577	2013		11.480					1976	165
	530-950	3000		12.210				AVMD	1978	163
N2O+Sr->Products	943-1073	3019		13.280					1977	161
N2O+Cl->N2+OCl	927-1031	16857		14.110					1956	162
N2O+Br->N2+BrO	876-973	18618		14.300					1956	162
N2O+I->N2+OI	876-973	19122		14.450					1956	162

Figure 1–5.1. N20 + Sn --> PRODUCTS

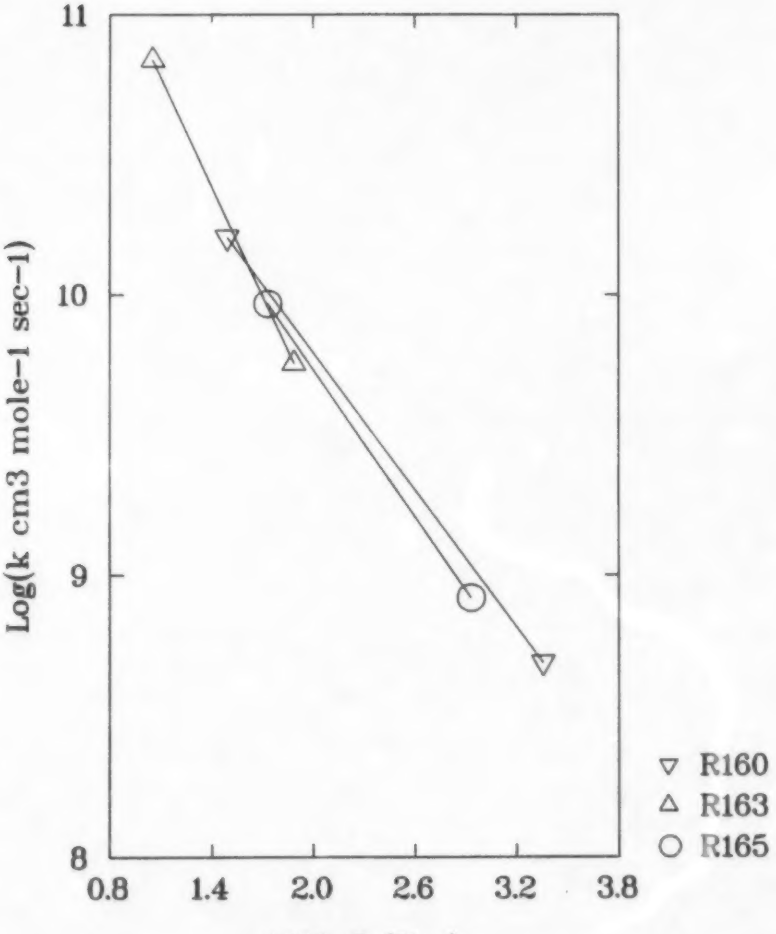
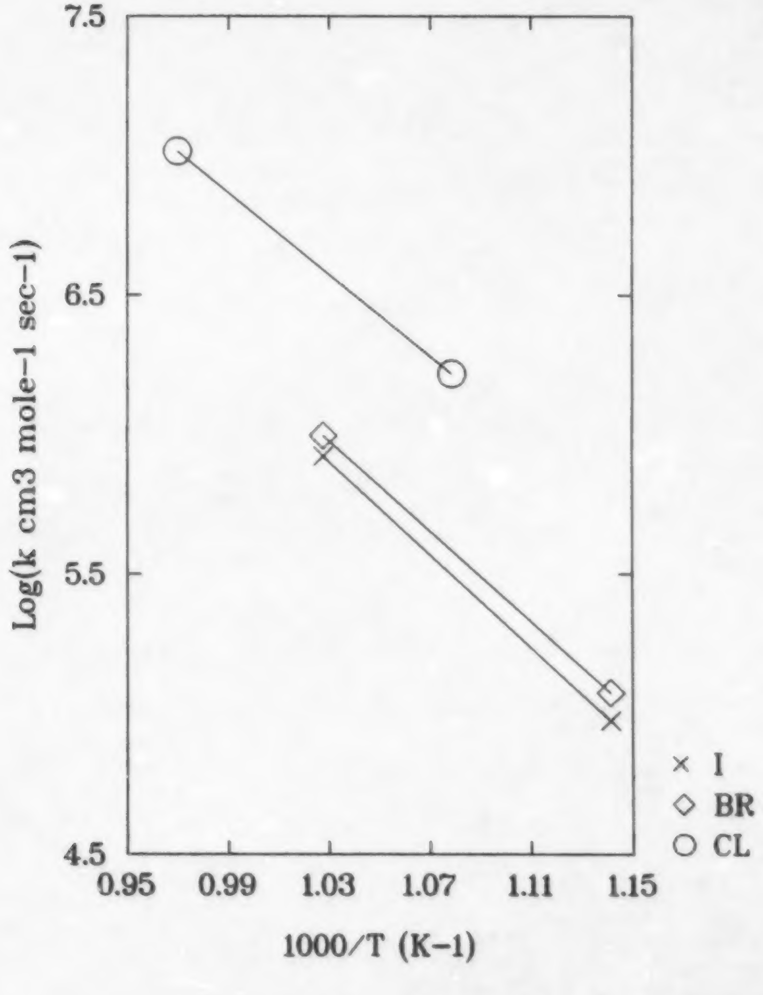


Figure 1–5.2. Reactions of N2O WITH HALOGENS

Data from REF 162



1-6.REACTIONS CONTRIBUTING TO FORMATION OF N_2O

(1) NO Dissociation

The formation of N_2O from NO as in reaction (1-6.1)

$$NO + NO \rightarrow N_2O + O \qquad (1\text{-}6.1)$$

has been verified as one of two initial, rate-limiting steps leading to the dissociation of nitric oxide. The second is reaction (1-6.2).

$$NO + M \rightarrow N + O + M \qquad (1\text{-}6.2)$$

Reaction (1-6.1) is dominant at low temperatures and high NO concentrations, while reaction (1-6.2) is dominant at high temperature and low NO concentrations[171].

The first study of the decomposition kinetics of nitric oxide under the high-temperature conditions attainable in a shock tube was that of Freedman and Daiber[172]. They measured the rate of disappearance of NO by UV absorption over the temperature range 3000-4300K and concluded that the principle reactions were reactions (1-6.2) and (1-6.3) with Ar as the bath gas.

$$NO + NO \rightarrow N_2 + O_2 \qquad (1\text{-}6.3)$$

Shortly thereafter, Wray and Fenberg[173] made a similar determination over a temperature range of 3000-8000K in a shock tube with UV absorption to measure the decreasing concentration of NO. Camac and Feinberg[174] studied the shock dissociation of NO in the course of a study of the rate of NO formation from reaction of N_2 and O_2. The NO concentration was determined by IR emission. They concluded that the principle modes of dissociation did not involve reaction (1-6.3), but rather reaction (1-6.1) and that Freedman and Daiber[172] had measured the rate of reaction (1-6.1) rather than reaction (1-6.3). This conclusion was reached on the basis of "preliminary" observations of IR emission of N_2O, and NO + O chemiluminescence.

There are several early measurements of the rate constant of reaction (1-6.1).[39,59,60,131,175-178] However, rate measurements related to the production of specific products were lacking and a wide range of uncertainty existed, as discussed in detail in the critical review of Baulch et al.[10]

Myerson[171] measured the formation of ground-state atomic oxygen behind shock waves in NO/Ar mixtures by atomic resonance absorption. By fitting his experimental data to a computer simulation, he confirmed the conclusion of Camac and Feinberg[174] and provided an Arrhenius expression of

$$k_{1-6.1} = 2.35\mathrm{x}10^{10}\exp(-14594/T)\ \mathrm{cm^3 mole^{-1} sec^{-1}}$$

over the temperature 2000-4000K. However, his value of the activation energy gave values of rate constants for reaction (1-6.1) at least one order of magnitude higher than those measured below 2000K.[178,179] Trung et al.,[180] studied the reaction over a relatively high temperature range (2700-4700K) using a shock tube and obtained an Arrhenius expression as follows,

$$k_{1\text{-}6.1} = 1.8\text{x}10^{11}\ \exp(-30455/T)\ \text{cm}^3\text{mole}^{-1}\text{sec}^{-1}.$$

Koshi and Asaba[181] studied NO decomposition over the temperature range 2700-3500K, using a shock tube with correction of the reaction time for boundary layer formation. Their value of the rate constant of reaction (1-6.1) of

$$k_{1\text{-}6.1} = 4.9\text{x}10^{12}\exp(-33765/T)\ \text{cm}^3\text{mole}^{-1}\text{sec}^{-1}$$

provides rate constants which are consistent with results obtained below 2000K by Wise and Frech[178] and McCullough et al.[179]

More recently, Thielen and Roth[182] monitored simultaneously the concentrations of N and O atoms in the post-shock region using atomic resonance absorption and obtained an Arrhenius expression for the rate constant for reaction (1-6.1) over the temperature range 2400-6200K as follows;

$$k_{1\text{-}6.1} = 9.0\text{x}10^{12}\exp(-35000/T)\ \text{cm}^3\text{mole}^{-1}\text{sec}^{-1}$$

This expression is in reasonable agreement with the results obtained by Koshi and Asaba[181].

A summary of the rate data of the reaction of NO with NO is given in Table 1-6.1 and the Arrhenius plots of the rate constants for this reaction are presented in Figure 1-6.1.

Table 1-6.1 Summary of Rate Data for Reaction NO + NO --> N2O + O

BGAS	PRESSURE (torr)	TEMP(K)	E/R(K)	LOGA cm3/mole*s	N	LOGK cm3/mole*s	METHOD	DATATYPE	YEAR	REF
			32346	12.511					1962	39
			32104	12.415					1955	131
			25663	9.544					1961	59
			27928	11.079					1961	176
			11070	12.000					1963	60
			32000	12.544					1966	175
		1200-2000	32104	12.110			CE	RECOM	1973	10
		1373-4273	43024	23.681	-2.5				1967	177
		1525				3.146			1952	178
Ar	760	1750-2100	32106	12.255				ESTIM	1977	179
		1912				5.663			1952	178
Ar	1049	2400-6200	35000	12.956			ST,V/UV A	AVMD,EP	1985	182
Ar	2-5	2600-6300	14594	10.371			ST,V/UV A	AVMD,RT	1973	171
Ar		2639-3399	33765	12.690					1979	181
Ne	1140-2660	2700-4700	30455	11.250	0.5		ST,MS	AVMD,RT/EP	1975	180

(2) Reactions of NO_2 with Nitrogen

Numerous studies have been reported on the reactions of NO_2 with N[11,58,60,183-192] and N_2[58,60,131,176]. These reactions produce N_2O according to reactions (1-6.4) and (1-6.5), respectively.

$$NO_2 + N \dashrightarrow N_2O + O \qquad (1\text{-}6.4)$$

$$NO_2 + N_2 \dashrightarrow N_2O + NO \qquad (1\text{-}6.5)$$

Figure 1–6.1a. NO + NO −−> N2O + O (1)

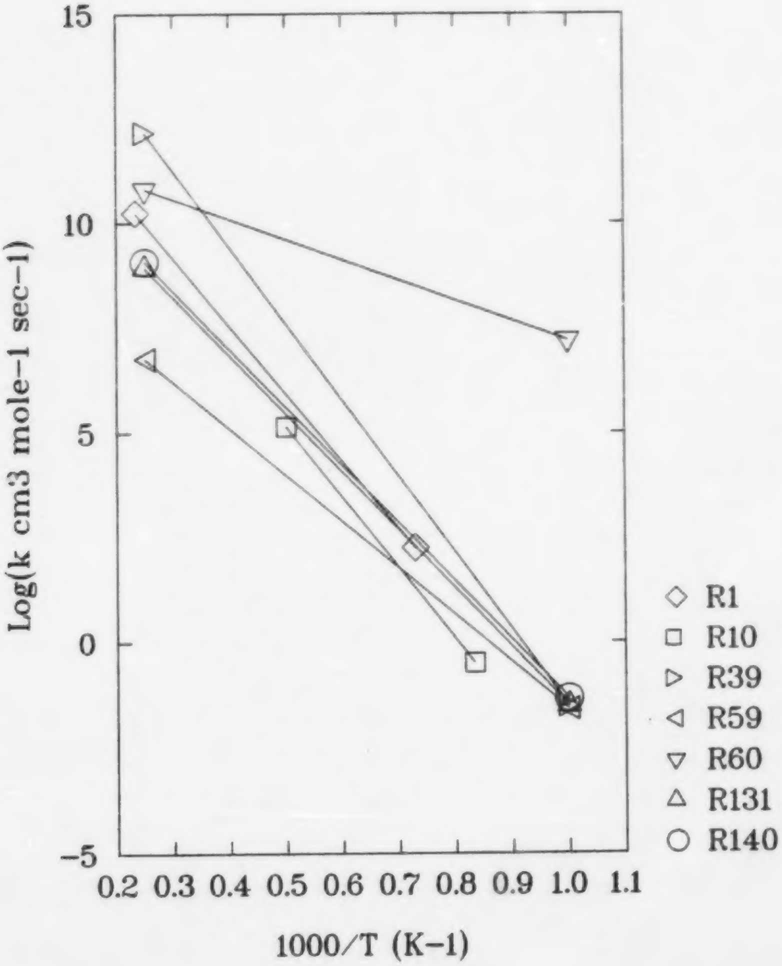
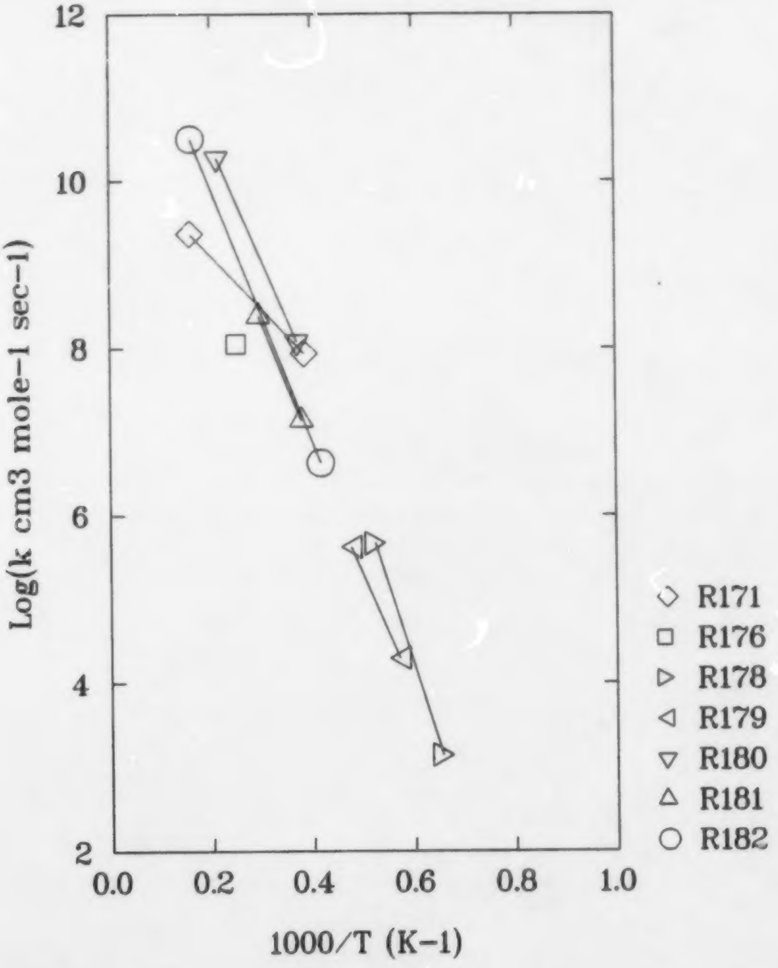


Figure 1–6.1b. NO + NO --> N2O + O (2)



Only one[58] determination of the activation energy of reaction (1-6.4) has been reported, providing an Arrhenius expression of

$$k_{1\text{-}6.4} = 1.15\text{x}10^{12}\exp(-4000/T)\ \text{cm}^3\text{mole}^{-1}\text{sec}^{-1}.$$

The other studies on reaction (1-6.4) reported only rate constants at room temperature with large discrepancies in the values from logk = 9.78 to logk = 13.1.

By contrast, early determinations of the rate constant of reaction (1-6.5) by three authors[58,60,131], are in good agreement.

A summary of the rate data of the reaction of N_2O with N and N_2 is given in Table 1-6.2.

Table 1-6.2 Rate Data of Reactions of NO2 with Nitrogen

TEMP(K)	E/R(K)	LOGA	LOGk	YEAR	REF
		cm3/mole *s			
NO2 + N --> N2O + O					
300			10.279	1961	183
300			13.000	1965	184
300			10.255	1961	185
300			13.079	1965	186
300			12.680	1965	187
298			10.114	1963	60
300			9.778	1957	188
300-500	4000	12.062		1963	58
300			10.477	1957	189
298			12.258	1982	190
298			11.925	1975	191
298			12.258	1987	11
298			12.258	1989	192
NO2 + N2 --> N2O + NO					
	42000	14.146		1963	58
<6000	41917	14.672		1955	131
	41917	13.342		1961	176
	41917	14.477		1963	60

1-7. REACTIONS OF HYDROGEN CYANIDE WITH OXYGEN ATOMS

It is generally accepted that hydrogen cyanide (HCN) is a key intermediate in the conversion of fuel nitrogen to NO.[193-195] The mechanism for converting fuel nitrogen to nitric oxide and molecular nitrogen in flames can be described globally as follows[196]:

$$\text{fuel N} \rightarrow HCN \rightarrow NH \rightarrow NO$$

$$NH + NO \rightarrow N_2 + OH$$

Recently, Kramlich et al.[9] studied the mechanism of N_2O formation in coal flames and showed that if HCN appears in the gas phase between 1150 and 1500K it will be partially converted to N_2O. The source of HCN may be either direct devolatilization, or a char gasification reaction. This suggests that N_2O which appears in coal flames may originate from the homogeneous reaction of gasified char nitrogen in the fuel-lean postflame region.

Studies of the kinetics of HCN are therefore of considerable interest in developing improved models for the combustion of fuels containing organically-bound nitrogen.

Among the reactions assumed to contribute to the oxidation of HCN in flames, the reaction with O-atoms, which can include several channels,

$$HCN + O \rightarrow CN + OH \qquad (1\text{-}7.1)$$

$$HCN + O \rightarrow NH + CO \qquad (1\text{-}7.2)$$

$$HCN + O \rightarrow NCO + H \qquad (1\text{-}7.3)$$

is thought to be of considerable importance[196].

An early study of Davies and Thrush[197] suggested that the most likely products of the reaction of O with HCN are NCO and H. This suggestion must be reassessed following the studies of Szekely et al.[198] and Louge and Hanson[199] which suggested that reaction channel (1-7.2) is also important. Further, the results of Roth et al.[200] are difficult to reconcile with the low temperature results of Davies and Thrush[197].

Studies of Roth et al.[200], Miller et al.[201], and Perry and Melius[202] have led to the determination of the overall coefficient $k_{1-7.1} + k_{1-7.2} + k_{1-7.3}$ and DeMore et al.[11] have recommended a value for the Arrhenius parameters as Log A = 12.78 (in units of $cm^3 mole^{-1} sec^{-1}$) and E/R=4000(K).

Perry and Melius[202] carried out their investigation by using two complementary but independent experimental techniques, laser photolysis-chemiluminescence to follow the decay of O atoms and laser photolysis-laser induced fluorescence to follow the formation of NCO. The combination of their experimental and theoretical results suggested that reaction(1-7.3) is the dominant channel at

840K (>66%), while reaction(1-7.2) is believed to account for nearly all of the remaining (<34%) of the products at this temperature. Reaction(1-7.1) should begin to become important only at temperatures greater than 2000K. By contrast, a study of the reactive deactivation of $O(^1D)$ atoms by HCN[203] shows that at room temperature the dominant channel for reaction leads to formation of $NH(a^1\Delta) + CO(X^1\Sigma^+)$ while less than 10% of the reactive encounters yield $OH(X^2\Pi) + CN(X^2\Sigma^+)$.

A summary of the rate data for the reaction of HCN with oxygen atoms is given in Table 1-7.1 and the Arrhenius plots for reactions (1-7.1), (1-7.2), (1-7.3), and the overall reaction (1-7.4)

$$HCN + O \text{ --> Products} \qquad (1\text{-}7.4)$$

are presented in Figures 1-7.1, 1-7.2, 1-7.3, and (1-7.4), respectively. It is obvious that large discrepancies exist in the published data for this reaction set.

Table 1-7.1. Summary of Rate Parameters for Reaction of HCN with Oxygen

BGAS	PRESSURE (torr)	TEMP(K)	E/R(K)	LOGA cm3/mole*s	N	LOGk cm3/mole*s	METHOD	DATATYPE	YEAR	REF
HCN + O --> CN + OH										
			7460	13.643			ST,V/UV A	RELAT,RT	1980	200
Ar		0300-2400	13386	9.433	1.6				1985	202
Ar	1277	1500-2600	7460	13.637			ST,V/UV A	RELAT,RT	1982	204
Ar	456-707	2000-2500	11000	13.699			ST,V/UV A	FIT,EP	1985	198
HCN + O --> CO + NH										
Ar		0300-2400	3824	8.734	1.2				1985	202
Ar	380-608	1800-2600	7740	13.342			ST,V/UV A	AVMD,EP/RT	1985	198
HCN + O --> NCO + H										
N2		0300-2400	3774	8.298	1.5				1985	202
Ar	456	1440				11.700	ST,V/UV A	RELAT,RT	1985	199
Ar	1277	1500-2600	7460	13.859			ST,V/UV A	AVMD,RT	1982	204
Ar		1800-2500	7460	13.863			ST,V/UV A	RELAT,RT	1980	200
Ar	1277	1800-2500	7460	13.863			ST,V/UV A	FIT,RT	1980	200
HCN + O --> Products										
		0200-0300	4000	12.780			CE	RECOM,	1987	11
Ar	75-200	0540-0900	4026	12.771			LF/FP/LIF	AVMD,RT/EP	1985	202
Ar	1277	1800-2500	7460	14.068			ST,V/UV A	FIT,RT	1980	200

Figure 1–7.1. HCN + O --> CN + OH

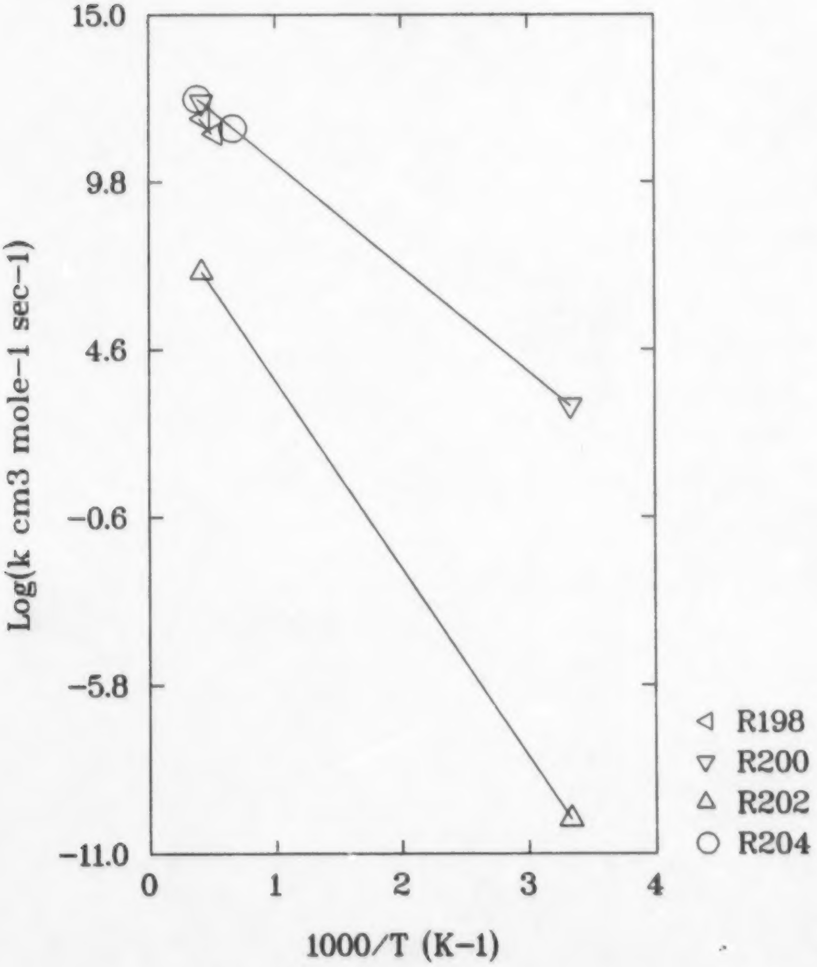


Figure 1–7.2. HCN + O --> CO + NH

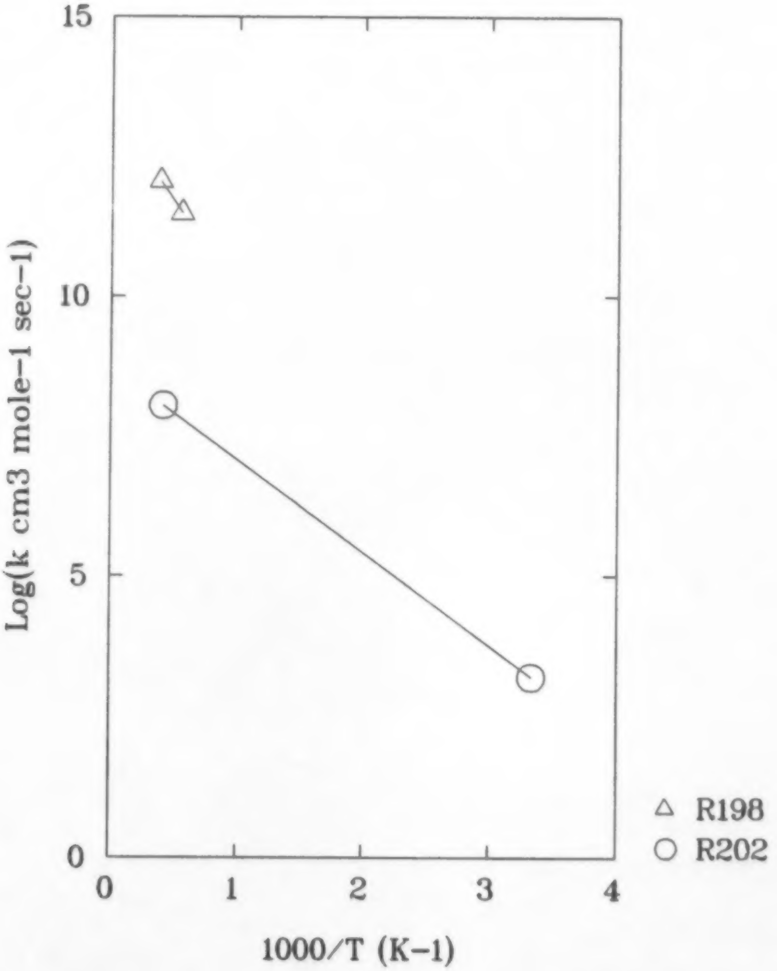


Figure 1–7.3. HCN + O ––> NCO + H

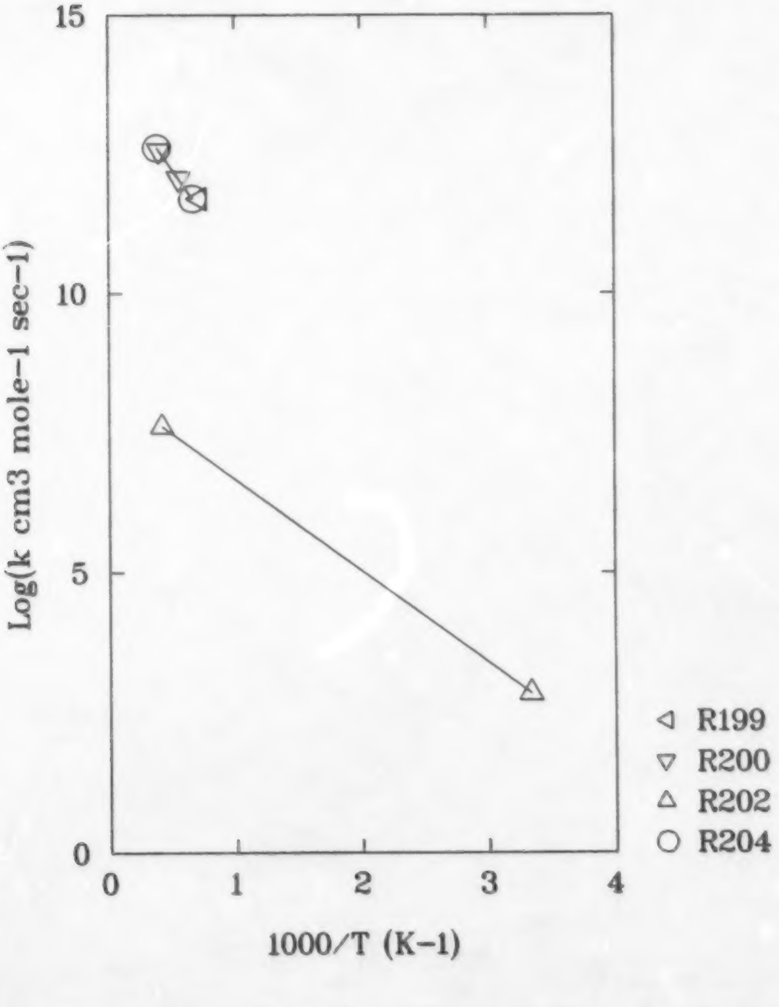
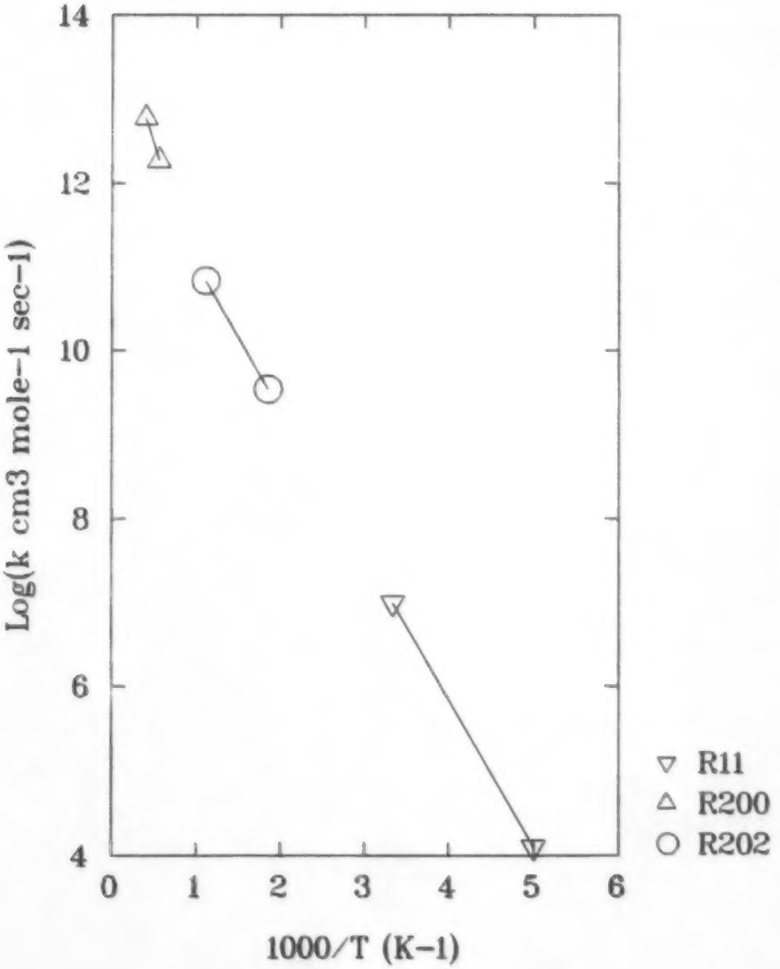


Figure 1–7.4. HCN + O --> PRODUCTS



1-8. REACTIONS OF NCO

Various investigators have concluded that the NCO radical is an important intermediate in fuel bound nitrogen combustion.[195,196,205] In order to model nitrogen chemistry in combustion systems, it is essential to explore all possible chemical reactions involving nitrogen that might enter into any model of the chemistry of these systems. While NCO chemistry has taken on an important role, surprisingly few reactions of NCO have been measured directly.

O and H atom reactions with NCO appear to play a key role in the conversion of HCN to NO and NH as in the following reactions:

$$O + HCN \longrightarrow NCO + H \qquad (1\text{-}7.3)$$

$$O + NCO \longrightarrow NO + CO \qquad (1\text{-}8.1)$$

$$H + NCO \longrightarrow NH + CO \qquad (1\text{-}8.2).$$

Schacke et al.[206], and Louge and Hanson[207], using a shock tube, studied reaction (1-8.1) and calculated values of the rate constant $8.91\text{x}10^{12}$ at a temperature of 298K and $5.61\text{x}10^{13}$ at 1450K (in units of $cm^3mole^{-1}sec^{-1}$). Lifshitz and Frenklach[208] estimated a value of 10^{13} $cm^3mole^{-1}s^{-1}$ for reaction (1-8.2) from their calculation over the temperature range 1400-2000K. Louge and Hanson[207] reported a rate constant of $5.37\text{x}10^{13}$ $cm^3mole^{-1}s^{-1}$ at 1490K for reaction (1-8.3). To the present, no value for the activation energy of either reaction (1-8.1) or (1-8.2) has been reported.

The reaction of NCO with O_2 provides another possible pathway to convert NCO to NO as shown in (1-8.3).

$$NCO + O_2 \dashrightarrow NO + CO_2 \qquad (1\text{-}8.3)$$

This could also be an important reaction in the atmospheric oxidation of HCN. Schacke et al.[206] reported a value of 7.94×10^{11} $cm^3mole^{-1}s^{-1}$ at 298K which indicated that this reaction was fairly important. However, results of Perry[209] suggest that under the conditions that exist in combustion environments or the stratosphere, it is unlikely that the reaction of NCO with O_2 will be important, since they did not observe its occurrence at room temperature or at a temperature of 662K. From this data, they estimated that the rate constant for reaction (1-8.3) was less than 6.02×10^{7} $cm^3mole^{-1}s^{-1}$ at 295K and less than 3×10^{7} $cm^3mole^{-1}s^{-1}$ at 662K.

The reaction of NCO with H_2 produces HNCO as shown in reaction (1-8.4),

$$NCO + H_2 \dashrightarrow HNCO + H \qquad (1\text{-}8.4)$$

Louge and Hanson[207] measured the rate constant of reaction (1-8.4) and gave a value of 1.26×10^{12} $cm^3mole^{-1}s^{-1}$. Perry [209] measured the rate constant for reaction (1-8.4) by using excimer laser photolysis-laser induced fluorescence and reported an Arrhenius expression of

$$k_{1-8.4} = 8.61\times10^{12}\exp[-(4529\pm770)/T]\ \mathrm{cm^3mole^{-1}sec^{-1}}.$$

Perry[209], and Cookson et al.[210] and Hancock and McKendrick[211] studied the reaction of NCO with NO by laser photolysis-laser induced fluorescence and have given a total rate constant for reaction (1-8.5).

$$\mathrm{NCO + NO \dashrightarrow Products} \qquad (1\text{-}8.5)$$

The value reported by Perry [209] for the temperature range 294-538K is

$$k_{1-8.5} = 1.02 \times 10^{13}\exp[(196 \pm 160)/T]\ \mathrm{cm^3mole^{-1}sec^{-1}}.$$

This value is in excellent agreement with the value of 2.05×10^{13} $\mathrm{cm^3mole^{-1}sec^{-1}}$ at 295K reported in other papers[210,211]. To the present no reports have been published for rate constants for reaction (1-8.5) at high temperature.

According to the value of $k_{1-8.5}$ obtained by Perry[209], a negative temperature dependence was observed for reaction (1-8.5). No pressure dependence was observed for the reaction. To the present, no measurement of the products of reaction (1-8.5) has been reported. The absence of a pressure dependence and the very large rate constant suggest that reaction (1-8.6)

$$NCO + NO \rightarrow N_2O + CO \qquad (1\text{-}8.6)$$

is the most likely channel for reaction (1-8.5). Other exothermic channels, such as,

$$NCO + NO \rightarrow N_2 + O + CO \qquad (1\text{-}8.7)$$

$$NCO + NO \rightarrow N_2 + CO_2 \qquad (1\text{-}8.8)$$

cannot be excluded, although reaction (1-8.7) is envisioned to occur on a triplet surface, possibly forming $N_2O(a^3\Sigma)$, and would have a substantial barrier to activation. Reaction (1-8.8) requires a 1-3 oxygen migration (four centre transition state). Although being energetically allowed, reaction(1-8.8) is anticipated to have an A factor that is significantly smaller than the A factor for a simple bond fission, i.e., as is the case for reaction (1-8.6).

All published studies on reactions of NCO with O, O_2, H_2 and NO are summarized in Table 1-8.1 and plotted in Figures 1-8.1, 1-8.2, 1-8.3, and 1-8.4, respectively.

Table 1-8.1. Summary of rate parameters for Reactions of NCO

BGAS	PRESSURE (torr)	TEMP (K)	E/R(K)	LOGA	LOGk	METHOD	DATATYPE	YEAR	REF
				cm3/mole*s					
NCO + O --> CO + NO									
Ar	3.8E3-1.8E6	1400-2000			13.000		ESTIM,	1980	208
Ar	456	1450			13.749	ST,V/UV A	FIT,RT	1985	199
Ar	5-250	298			12.950	FT,V/UV A	AVMD,RT	1974	206
NCO + O2 --> CO2 + NO									
		295-662	-369	7.236		LP,LIF	ULMD,RT	1986	209
Ar	2-250	298			11.900	FT,V/UV A	AVMD,RT	1974	206
	10-372	662			7.478	LP,LIF	ULMD,RT	1986	209
NCO + NO --> Products									
Ar	25-100	294-538	-196	13.009		LF/FP,LIF	AVMD,RT	1985	205
Ar	2-10	295			13.312	LF/FP,LIF	AVMD,RT	1985	210
N2O	5	295			13.312	LF/FP,LIF	AVMD,RT	1986	211
NCO + H --> NH + CO									
Ar	494	1490			13.730	ST,V/UV A	FIT,RT	1984	207
NCO + H2 --> HNCO + H									
Ar	494	1490			13.100	ST,V/UV A	FIT,RT	1984	207
Ar	75-100	592-913	4529	12.935		LF/FP,LIF	AVMD,RT	1985	205

The very fast kinetics observed for the reaction of NCO with NO suggests that the production of nitrous oxide by reaction (1-8.7) must be considered an additional alternative channel, and may be one source of nitrous oxide in nitrogen-containing fuel flames. Reaction (1-8.6) should be of particular importance in propellant chemistry where propellants such as HMX give species such as NO_2, HCN, N_2O, and H atoms in high initial concentrations[212]. Among other reactions, the fast decomposition of N_2O implies that reaction (1-8.6) may be intimately involved in the regeneration of nitrous oxide in propellant chemistry. Recently, Kramlich et al.[9] concluded that the formation of N_2O is principally through reactions (1-8.1) and (1-8.7).

Figure 1–8.1. NCO + O --> CO + NO

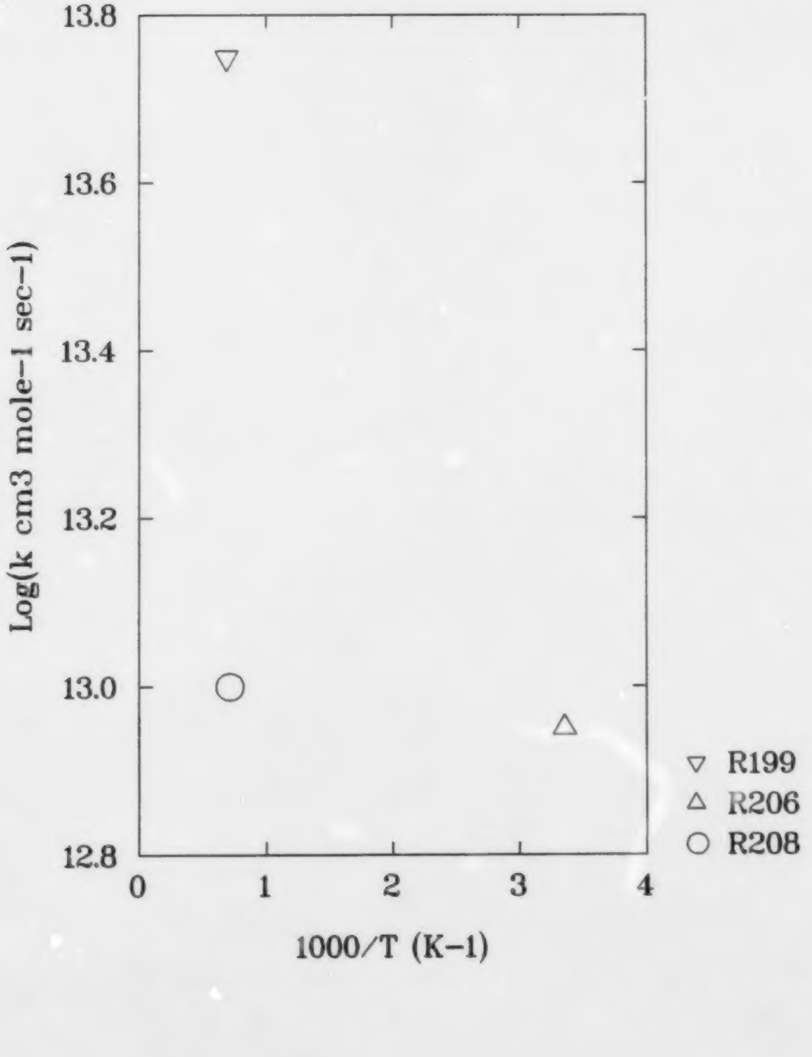


Figure 1–8.2. NCO + O2 --> CO2 + NO

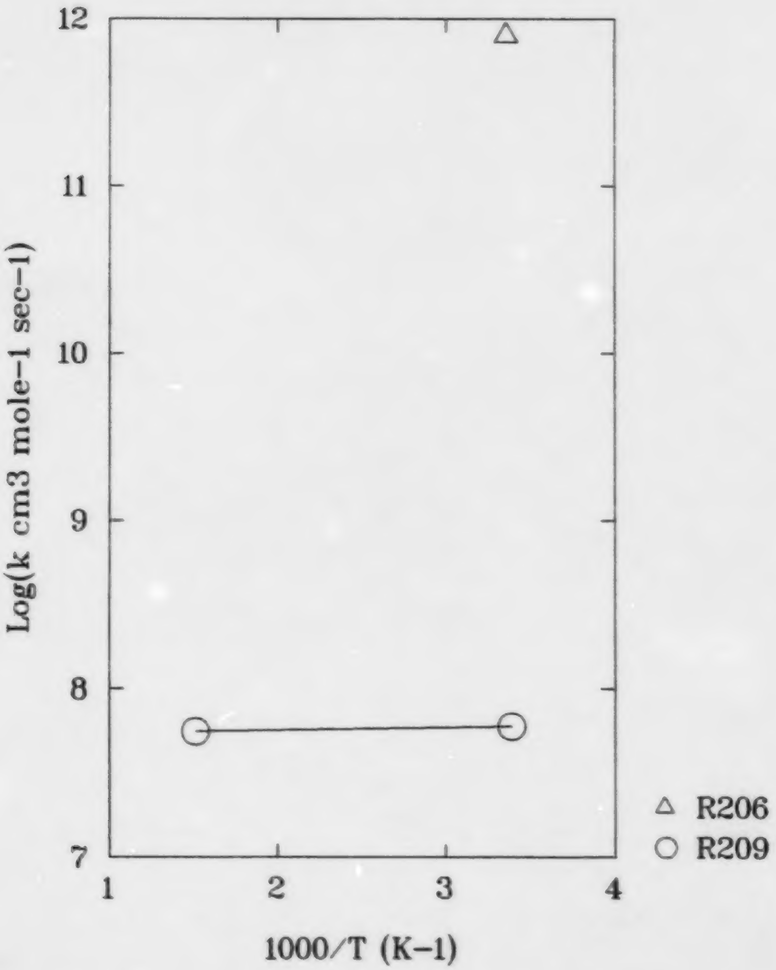


Figure 1–8.3. NCO + H2 --> HNCO + H

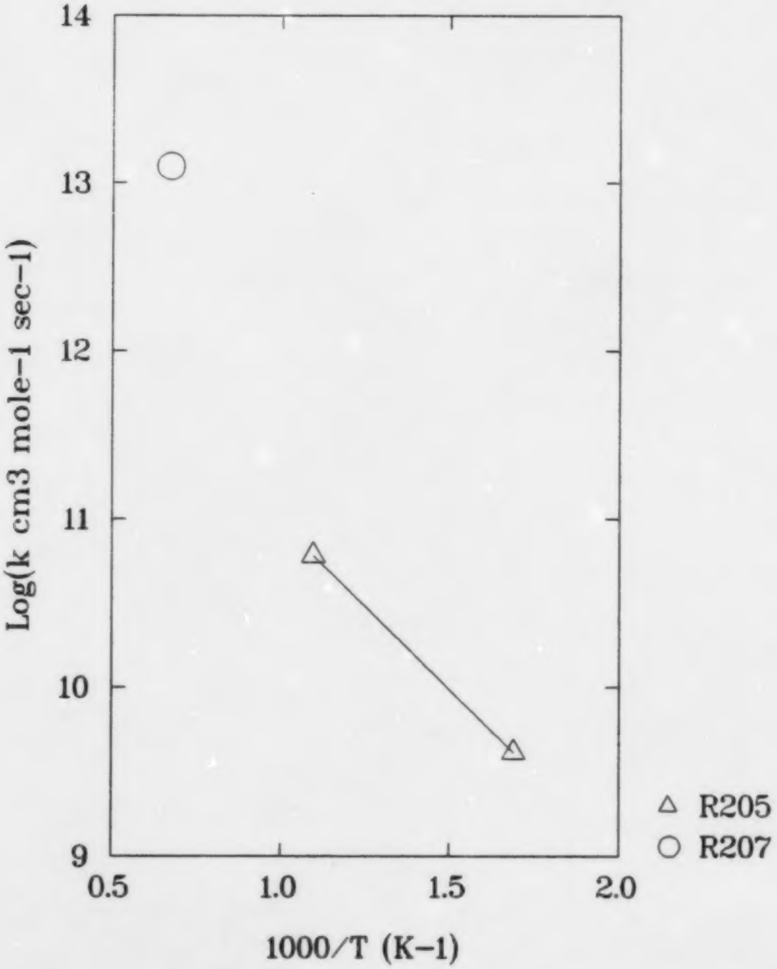
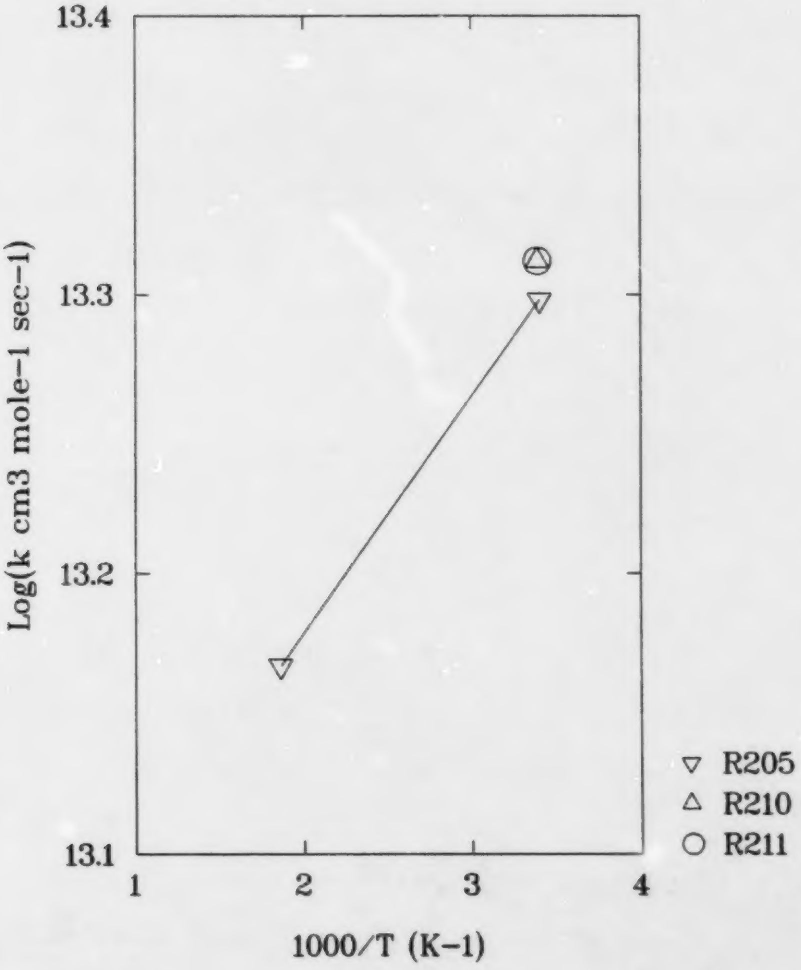


Figure 1–8.4. NCO + NO --> PRODUCTS



1-9. REACTIONS OF NO WITH HYDROGEN

Nitric oxide is an important constituent of many combustion systems. It plays a dominant role in rocket motors employing packaged fuels and oxidants and reactions occurring in air-breathing engines. The reactions in air breathing engines, while very much subsidiary to the major chemical processes in terms of energy release, are nevertheless of importance since the nitrogen oxide effluent is considered to be a major contributor to atmospheric pollution. The kinetics of nitric oxide removal are of most interest in studies of nitrogen chemistry in combustion and air pollution. A principal mechanism for removal of NO is provided by reactions (1-9.1) and (1-9.2)[213]

$$NO + O \longrightarrow N + O_2 \qquad (1\text{-}9.1)$$

and

$$N_2 + O \longrightarrow N + NO \qquad (1\text{-}9.2)$$

generally called the Zel'dovich mechanism. The additional reaction

$$NO + H \longrightarrow N + OH \qquad (1\text{-}9.3)$$

is also of importance in combustion systems, particularly during fuel-rich operation. Reactions (1-9.1) to (1-9.3) are sometimes referred to as the extended Zel'dovich mechanism[214].

Quantitative measurements of the rate constant of reaction (1-9.3) in the high temperature range (2220-4500K) were first reported in the Proceedings of the 15th Symposium (International) on Combustion[215-218]. In these four papers, investigations were carried out in shock-tube heated mixtures of nitric oxide, hydrogen, and argon. Reaction (1-9.3) was considered to be the critical propagation/branching reaction. Flower et al.[217] and Koshi at al.[215] monitored the 5.3μ emission of NO, while Duxbury and Pratt[216] and Bradley and Craggs [218] monitored the 236 nm and 226 nm absorption of NO and 306.4 nm absorption of OH. In the studies of Flower et al. and Duxbury and Pratt attention was paid to the influence of $k_{1-9.3}$ on the overall reaction rate, and $k_{1-9.3}$ was determined by computer simulation, fixing all other elementary reaction rate constants including those of the initiation reactions. Bradley and Craggs[218] discussed the reaction and suggested three plausible initiation reactions as follows,

$$H_2 + M \longrightarrow H + H + M \qquad (1\text{-}9.4)$$

$$H_2 + NO \longrightarrow H + HNO \qquad (1\text{-}9.5)$$

$$NO + NO \longrightarrow N_2O + O \qquad (1\text{-}6.1)$$

They evaluated their results on the basis of these three initiation reactions but were not able to determine which of the reactions was the most important. Koshi et al.,[215] found, over a wide range of the initial concentrations of nitric oxide and hydrogen, that their experimental results could not be simulated completely by varying

$k_{1-9.3}$ only. As a result, they determined $k_{1-9.3}$ using a steady-state treatment. They suggested that an initiation reaction producing atomic hydrogen was the most influential and that reaction (1-9.5) was considered to be the most probable candidate. Their value of the rate constant of reaction (1-9.5) was found to be somewhat larger than the value obtained in flame experiments[219-221].

Only a few papers on the reactions of NO with H and H_2 have been published[179,222,223] since the early reports. From a review of the available literature, McCullough et al.[179] recommended a value of $1.71\times10^{14}\exp(-24558/T)$ $cm^3mole^{-1}sec^{-1}$ for the rate constant for reaction (1-9.3).

A summary of rate data for reactions (1-9.3) and (1-9.5) is given in Table 1-9.1 and presented in Figure 1-9.1 and 1-9.2.

In the low temperature range, the reaction of NO with H follows a quite different mechanism as shown in reactions (1-9.6) to (1-9.9).

$$NO + H + M \dashrightarrow HNO + M \qquad (1\text{-}9.6)$$

$$NO + H + M \dashrightarrow HNO^* + M \qquad (1\text{-}9.7)$$

$$HNO^* + M \dashrightarrow HNO + M \qquad (1\text{-}9.8)$$

$$HNO^* \dashrightarrow HNO + h\mu \qquad (1\text{-}9.9)$$

Numerous studies of the formation of HNO from NO and H have been carried out at or near room temperature[215,219,225-236]. Only two

Figure 1–9.1. NO + H --> OH + N

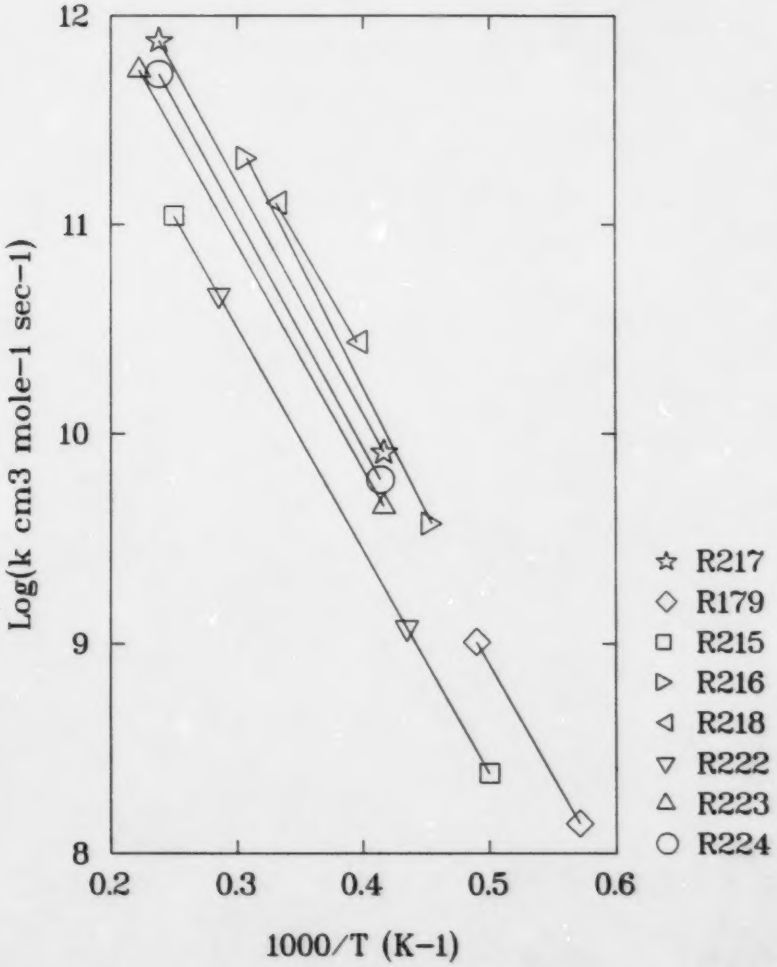
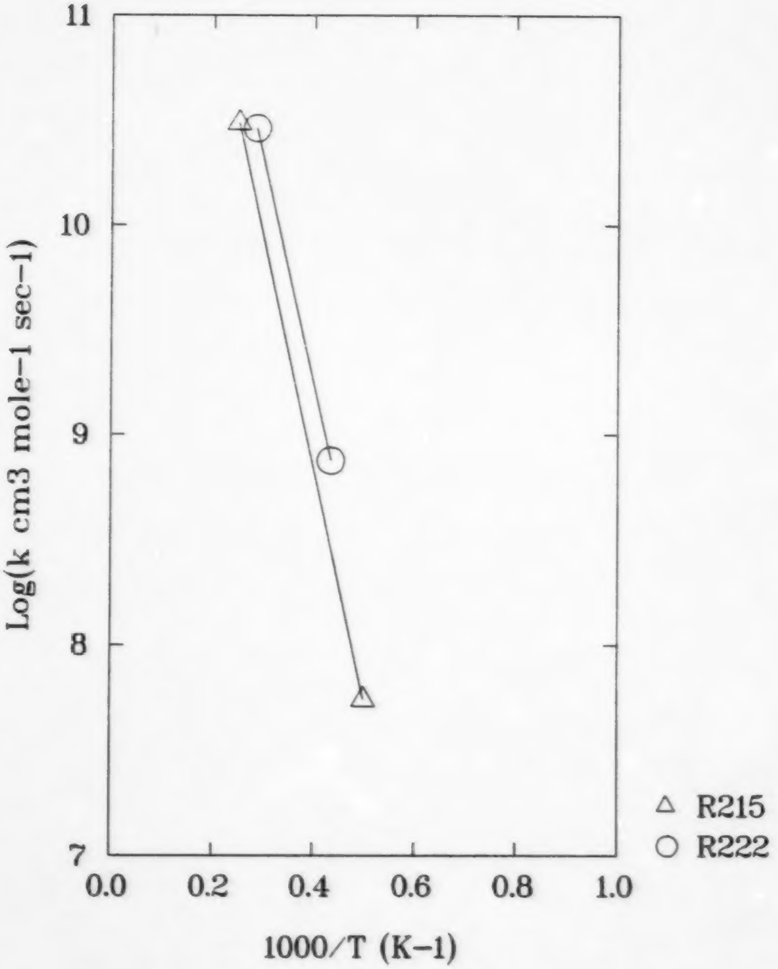


Figure 1-9.2. NO + H2 --> H + HNO



investigations[225,226] varied the temperature, which resulted in the observation of a slight negative activation energy. The third body efficiencies of various gases for the reaction were reported in several publications[229,215,232,234]. Recently, Forte [231] studied the reaction as a function of inert gas pressure ($M=N_2$,Ar) from 0.5-1200 atm at 303 and 313K. The transition pressure was found to be approximately 60 atm and the high pressure limiting rate constant attained at pressures over 400 atm was calculated to be

$$\log k_{1\text{-}9.6} = 14.7 \pm 0.35 \text{ cm}^3\text{mol}^{-1}\text{sec}^{-1}$$

at 313K for $M=N_2$.

A summary of the rate data of reaction (1-9.6) is presented in Table 1-9.2 and Figure 1-9.3. The rate constants $k_{1\text{-}9.6}$ at different bath gases published by Ahumada et al.[229] are presented in Figure 1-9.4.

Table 1-9.1 Summary of Rate Data for High Temperature Reactions of NO with Hydrogen

BGAS	PRESSURE (torr)	TEMP(K)	E/R(K)	EERR (%)	LOGA cm3/mole*s	METHOD	DATATYPE	YEAR	REF
				NO + H --> OH + N					
Ar	760	1750-2040	24759		14.241	FT,GC	AVMD,RT	1977	179
Ar	760	1750-2040	24558		14.233	CE	RECOM,	1977	179
Ar	20-200	2000-4000	24507		13.700	ST,V/UV A	FIT,RT	1975	215
Ar	684-3420	2200-3250	24558		14.415	ST,V/UV A	FIT,RT	1975	216
Ar	20-200	2300-3500	24509		13.700		FIT,	1976	222
Ar	190-471	2400-4200	25413		14.508	ST,V/UV A	FIT,RT	1976	217
Ar	25	2400-4500	24759	2.0	14.127	ST,IR	AVMD,RT	1975	223
Ar	190-471	2415-4200	25413	1.0	14.346	ST,IR	FIT,RT	1977	224
Ar	7-20	2530-3020	23935		14.544	ST,V/UV A	FIT,RT	1975	218
				NO + H2 --> H + HNO					
Ar	20-200	2000-4000	27778		13.500	ST,V/UV E	FIT,RT	1975	215
Ar	20-200	2300-3500	24509		13.500	ST,V/UV E	FIT,RT	1976	222

Table 1-9.2. Summary of Rate Data for Low Temperature Reaction NO + H + M --> HNO + M

BGAS	PRESSURE (torr)	TEMP(K)	E/R(K)	LOGA cm6/mole2s2	LOGk	METHOD	DATATYPE	YEAR	REF
H2	100-145	285-390	-272	15.949		FP,V/UV E	AVMD,RT	1973	121
H2		293			16.300			1967	235
H2		293			16.140			1971	227
H2		294			16.174	FT		1962	233
H2		294			16.050			1963	234
H2		294			15.680	FT		1961	219
H2	300	298-477	-363	15.664		LF/FP,CHEMI	AVMD,RT	1977	226
H2	100-1500	298			16.146	S/LF,V/UV A	AVMD,RT	1971	227
H2	100-900	298			16.223	S/LF,V/UV A	AVMD,RT	1979	228
H2	57-602	298			16.360	LF/FP,V/UV A	AVMD,RT	1972	229
H2	50-300	298			16.193	LF/FP,CHEMI	AVMD,RT	1977	230
H2		Room			16.330				236
N2	912000	313			14.699	LF/FP,V/UV A	RT	1981	231
N2	3.0	392			12.155	FT,CHEMI	AVMD,RT	1975	237
He	58-604	298			16.193	LF/FP,V/UV A	AVMD,RT	1972	229
Ne	107-601	298			15.882	LF/FP,V/UV A	AVMD,RT	1972	229
Ar	57-599	298			16.152	LF/FP,V/UV A	AVMD,RT	1972	229
Ar	1-600	298			16.146	LF/FP,V/UV A	AVMD,RT	1971	238
Ar	76000	313			14.176	LF/FP,V/UV A	RT	1981	231
Ar	3	392			15.940	FT,CHEMI	AVMD,RT	1975	237
Kr	99-605	298			16.292	LF/FP,V/UV A	AVMD,RT	1972	229
		Room		16.141			225		

Figure 1–9.3a. NO + H + H2 --> HNO + H2

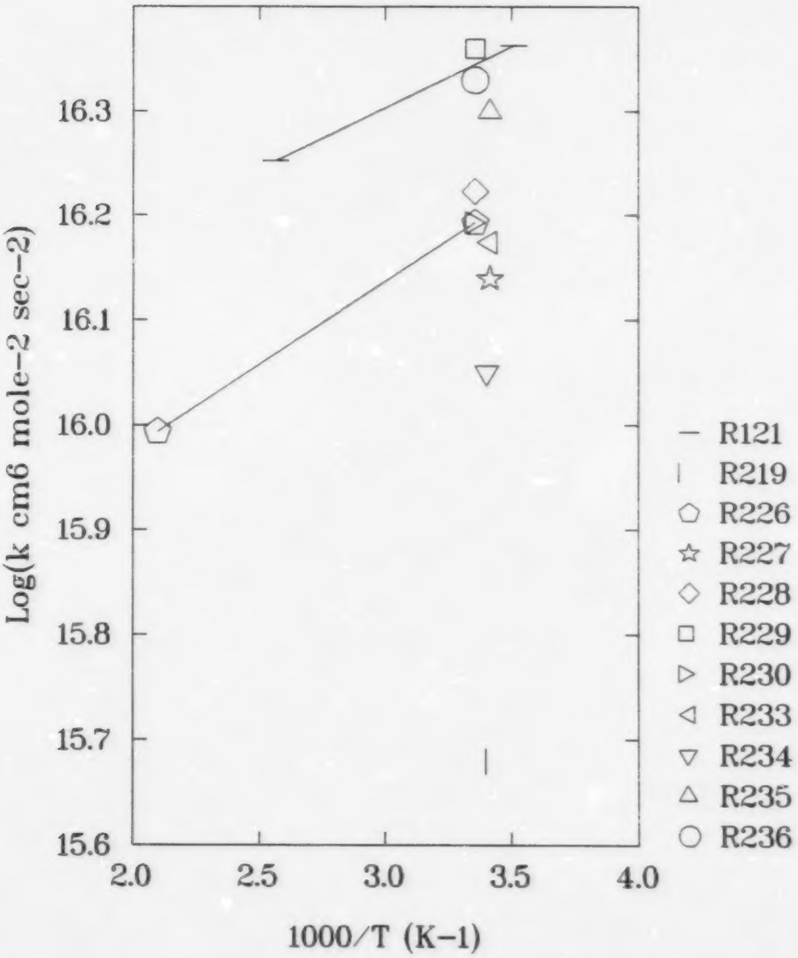


Figure 1–9.3b. NO + H + N2 --> HNO + N2

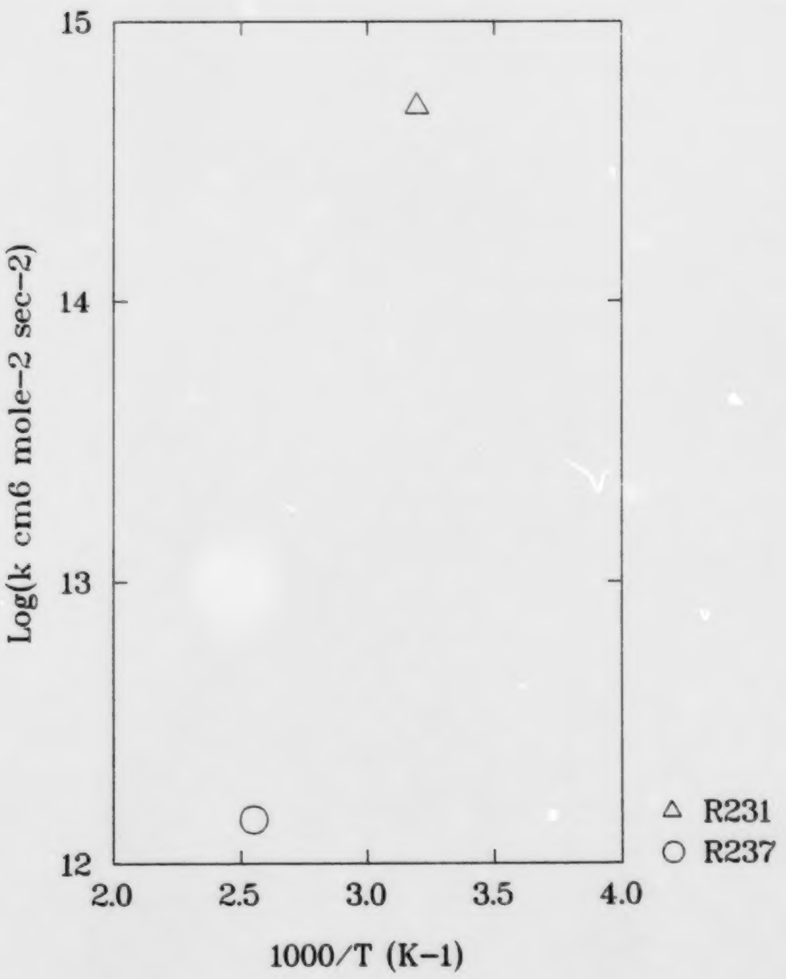


Figure 1-9.3c. NO + H + Ar --> HNO + Ar

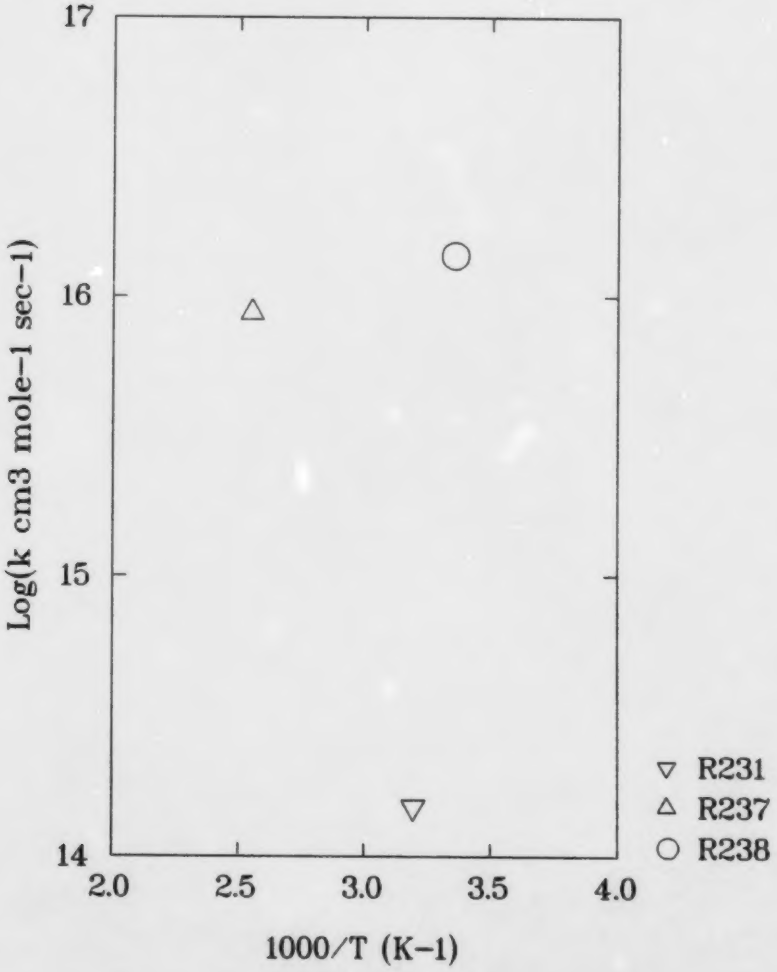
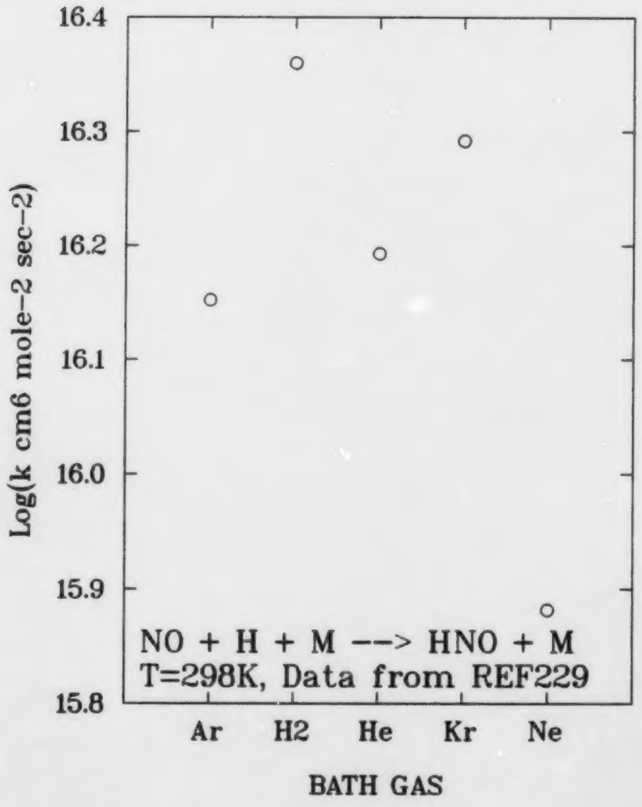


Figure 1–9.4. Logk vs Bgas



PART II. GLOBAL REACTIONS

2-1. REACTIONS OF NO WITH CARBONACEOUS MATERIALS

Investigations of the reaction of NO with carbonaceous materials are important since they may contribute to a mechanism for control of NO emission.

Pereira and Beer[240,241] have demonstrated NO reduction by char in fluidized bed coal combustors. They observed that NO formed in the lower part of the bed was significantly reduced in the upper part of the bed as well as in the free board. Thus the overall NO emission level may be determined by the relative importance of the in situ formation and destruction processes. The non-catalytic reduction of nitric oxide by char formed in situ (char-consuming reduction of NO) has been considered to be the most important nitric oxide destruction reaction, and a number of kinetic investigations have been reported[240-259]. In recent years, the deleterious effect of N_2O emission has been considered, therefore, the formation of N_2O in the reduction of NO by char should be examined carefully.

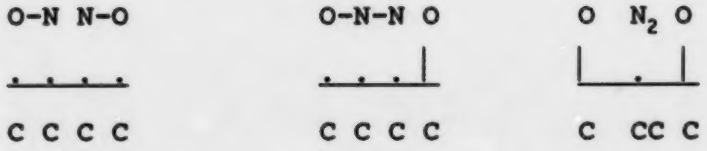
Early investigations of the reaction of NO with char were carried out by Shelef and Otto (1969)[242], Watts (1958)[243], and Bedjai et al.,(1958).[244] Watts [243] studied the kinetics of the reaction between charcoal and NO in the temperature range 578 to

723K. He found that the reaction obeys a first-order rate law over an NO pressure range of 1.4 to 22 torr. The major gaseous products were N_2, CO, CO_2 and residual NO. A mass spectrometric analysis of the products of the reaction at 723K, in which 77% of the NO was reduced, revealed the presence of 2% N_2O. Estimation of the total amount of oxygen bound to the charcoal surface in the form of chemisorbed oxygen or adsorbed products was made from the analytical data. They suggested the first step of the reaction to be adsorption of NO on the surface followed by reduction of the NO to give chemisorbed oxygen, and nitrogen which later desorbed, i.e.,

$$\mathrm{NO} + 2\mathrm{C} \dashrightarrow \mathrm{C(N)} + \mathrm{C(O)} \qquad (2\text{-}1.1)$$

$$\mathrm{C(N)} + \mathrm{C(N)} \dashrightarrow (\mathrm{N_2})_g + 2\mathrm{C} \qquad (2\text{-}1.2)$$

where C represents a surface carbon, C(N) and C(O) adsorbed nitrogen and oxygen atoms. Their observation of N_2O formation led them to suggest the following mechanism in which an adsorbed NO molecule could give up its oxygen to the surface,



Recently, Levy et al.,(1981)[245] studied NO/char reactions using a laminar flow furnace in a temperature range of 1250-1750K, under conditions similar to those in pulverized coal combustion. Levy et al.,[245] also made complimentary time-resolved experiments in a packed bed reactor at temperatures of 800 to 1200K. These results were used to provide mechanistic insight into the reactions between NO and carbon. They obtained the effective rate of the NO/char reaction over the temperature range 1250 to 1750K, to be,

$$(d[NO]/dt)=4.18\mathrm{x}10^{4}\exp(-34.70\mathrm{Kcal}/RT)A_{E}P_{NO}\mathrm{moles\ sec}^{-1}$$

where A_E is the external surface area of the char in m^2/gm and P_{NO} is the pressure of NO in atmospheres. The rate of reaction was found to be retarded by water vapour and enhanced by CO by amounts that decrease with increasing temperature. From their observations they proposed the following kinetic scheme. The reduction of NO by carbon occurs through dissociation of NO on the surface with a rapid diffusion of the dissociated atoms to form N_2. The oxygen produced by the dissociation is strongly chemisorbed and inhibits further reaction. The chemisorbed oxygen can either desorb to produce CO or react with CO to form CO_2, i.e.,

$$C(O) \dashrightarrow (CO)_g \qquad (2\text{-}1.3)$$

$$C(O) + CO \dashrightarrow (CO_2)_g + C \qquad (2\text{-}1.4)$$

The inhibition of the NO/C reaction by H_2O was explained by the formation of the chemisorbed oxygen layer. The rate enhancement by CO was explained by the removal of the chemisorbed oxygen layer by reaction with CO. With increased temperature, enhancement of the rate of activated decomposition of the chemisorbed oxygen by reactions such as (2-1.3) decreased the steady-state coverage of the surface by the oxide layer.

A parallel study in the same laboratory by Chan et al.,[246] which was carried out under the conditions relevant to fluidized bed combustion over the temperature range 723-1173K, directly supports the above mechanism. They found that the dominant products were N_2, CO and CO_2. They found no evidence of the formation of N_2O in the temperature range explored. This was in contrast to earlier studies [242-244] which show evidence of N_2O as a possible intermediate in the direct reduction of NO with the carbon surface.

Another relevant result in the work of Chan et al.[246] was the observation that for bed temperatures below 800K passage of NO through the bed result in a transient reaction between NO and C which decreased slowly to zero. During the transient reaction period N_2 was found in the product gases in amounts equal to that expected from the decrease in NO concentration. By contrast the amount of oxygen appearing as CO and CO_2 was significantly less than that expected from the decrease in NO, supporting the postulate that the oxygen was being chemisorbed. Also, they obtained the kinetic parameters of the reaction of NO with carbonaceous materials such as graphite and dashed char for various NO and CO concentrations, temperatures, and carbon types. The reaction rate per unit total surface area is found to be first order in NO, to have an apparent activation energy of 44 kcal/mole for temperatures higher than 873K, to be enhanced by the presence of CO, and to vary by approximately an order of magnitude between graphite and coal chars.

Furusawa et al.[247-250] determined the reaction rate constants k for the reduction of NO by char and by activated carbon at an NO concentration of 962ppm (for temperatures below 1073K) and for 339ppm for temperatures above 1073K over a range of reaction temperatures from 773 to 1118K and a range of residence times from 2.3×10^{-3} to 3.3×10^{-1} sec, by using a fixed-bed, isothermal tubular flow reactor. The Arrhenius expression obtained was

$$k = 3.5\times10^{14} \exp(-29700/T)\ s^{-1}.$$

They found that the reaction rate equation was first order with respect to the NO concentration over the entire range of temperatures studied, and that the activation energy increased at temperatures above about 953K. For the reactions where char was present, the gaseous reaction products that were formed at each temperature were analyzed by Furusawa et al.[247] It was found that at lower temperatures N_2 and CO_2 were formed, while at temperatures above that corresponding to the increase in the activation energy, N_2, CO, and CO_2 were formed.

In another study, Furusawa et al.[248] examined the reduction of nitric oxide during combustion of coal char in a fluidized-bed combustor with respect to: (1) char-consuming and (2) char-catalyzed reactions. The relative importance of the two reactions was determined by measuring detailed material balances. They suggested that at high temperatures ($973K<T<1194K$) and $P_{CO}/P_{NO} = 0$, the dominant mechanism was a carbon-consuming reaction, i.e., through reaction (2-1.1), (2-1.2) and (2-1.3), while at low temperatures and $P_{CO}/P_{NO} = 0$, the dominant mechanism is also carbon-consuming but the adsorbed oxygen would react with NO to form N_2 and CO_2, through reactions (2-1.1), (2-1.2) and (2-1.5),

$$C(O) + NO \dashrightarrow CO_2 + 1/2N_2 \qquad (2\text{-}1.5)$$

Under conditions in which $P_{CO}/P_{NO} > 1$, the dominant mechanism involves a catalytic reaction (carbon not consumed). Adsorbed oxygen reacts with CO to form CO_2 and a free active carbon site, C_f, through reactions (2-1.1), (2-1.2) and (2-1.6).

$$C(O) + CO \dashrightarrow CO_2 + C_f \qquad (2\text{-}1.6)$$

A detailed discussion on the catalytic reaction of NO with CO by char is given in Section 2-2.

The work of Glass and Wendt[251] suggests that the heterogeneous reaction of NO on a char surface is too slow to account for the observed experimental NO reduction. Rather, Glass and Wendt's data suggest that post flame reactions in the gas phase dominate in the destruction of NO in coal combustion. However, their analysis did not include the possible contribution of soot particles, which are clearly observed under similar conditions during the combustion of pulverized coal[252]. Cheng [253] reported an experimental study conducted to evaluate the global rates of the reaction of NO with carbon black particulates at flame temperatures (1500-2000K) by using a single shock technique. The intrinsic rate coefficient, k, was determined, based on a first-order reaction, according to the relationship:

$$k=Ln([NO]_i/[NO]_f)V/(AtRT)$$

where $[NO]_i/[NO]_f$ is the ratio of initial NO concentration to the final NO concentration after heating at temperature T and reaction time t, A is the total B.E.T. surface area of carbon blacks and V is the volume in the reflected shock wave region. They found $k = 4.4x10^{-4}exp(-19.18kcalmol^{-1}/RT)mol/m^2sPa$. This result indicates that the NO removal rates on carbon blacks are much greater than rates determined previously for NO removal on char[245,254]. The role soot particles play in NO destruction mechanisms in a pulverized coal flame may be significant. The major reaction products are CO and CO_2, with the concentrations of CO_2 increasing with temperature.

Two mechanisms can be envisioned for the production of CO and CO_2 during the reaction of NO on carbon black. One is a dual site dissociative (DSD) mechanism in which one NO molecule occupies two adjacent sites and the N-O bond ruptures. The other is the dual site nondissociative adsorption (DSND), which requires two molecules and two adjacent carbon sites. No direct evidence has been reported on which mechanism dominates at high temperatures. No N_2O was observed in the experiments of Cheng et al.[253].

Mochida et al.[255] has studied the reduction of NO in flue gases with polyacrylonitrile-based active carbon fibres (PAN-ACF) activated with sulphuric acid at 423-632K, using a circulating flow reactor. They reported that NO (0.67mmol) was completely removed via reduction with 1g activated carbon under optimum conditions in 210 and 60 min at 423 and 623K, respectively. N_2 was formed as NO was removed. They found that the activation of PAN-ACF with sulphuric acid produced the oxidative site for activation of nitric oxide and that the reaction between two molecules of such activated NO on carbon surfaces is the rate-determining step. At 423K the reduction of the two activated NO molecules by carbon to a nitrogen molecule leaves oxygen on the carbon surface. They also found that at 623K the oxygen is evolved as CO and CO_2. No N_2O was reported to be present in the products.

2-2. CATALYTIC REACTIONS OF NO WITH CO

(1). Catalytic Reduction of NO by CO on Char Surfaces

The significant reduction of nitric oxide emission observed under fuel-rich conditions suggests an important role for surface-catalyzed reduction of NO by carbon monoxide. Levy et al.[245] found that the addition of CO slightly enhanced the rate of reduction of NO by char. The ratio of the rate constant of NO reduction with addition of 1.4% CO, k_{CO} to that without addition of CO, k was found to be 1.28 at 1300K and 1.14 at 1600K. They suggested that the increase in rate may be a consequence of either a surface catalyzed NO/CO reaction as in (2-2.1)

$$NO + CO \rightarrow CO_2 + 1/2N_2 \qquad (2\text{-}2.1)$$

or an increase in active sites by the reaction of CO with surface oxides as in (2-2.2).

$$CO + C(O) \rightarrow CO_2 + C_f \qquad (2\text{-}2.2)$$

$$NO + C_f \rightarrow C(O) + 1/2N_2 \qquad (2\text{-}2.3)$$

The observation that the enhancement of NO/C reaction by CO decreases with increasing temperature favours the latter explanation. As the temperature is increased the rate of loss of chemisorbed oxygen through formation of CO by the reaction (2-2.4)

$$C(O) \dashrightarrow CO \qquad (2\text{-}2.4)$$

rapidly increases; the concentration of chemisorbed sites will therefore decrease and the importance of the activation of the sites by reaction (2-2.2) diminishes.

A parallel study in the same laboratory by Chan et al.[246] found that the NO conversion increases with the CO/NO ratio and approaches an asymptotic value at high CO/NO values. They derived a simple Langmuir-Hinshelwood model for the reaction of NO with carbon in the presence of CO by using reactions (2-2.1) to (2-2.4). An empirical fit of their data with qualifications was obtained by assigning the follow values:

$$k_{2\text{-}2.1} = 2.1\times10^{-2}\exp(-26{,}000/RT)\,\text{mole sec}^{-1}\text{ cm}^{-2}\text{ atm}$$
$$k_{2\text{-}2.2} = 7.4\times10^{-5}\exp(-19{,}000/RT)\,\text{mole sec}^{-1}\text{ cm}^{-2}\text{ atm}$$
$$k_{2\text{-}2.3} = 1.5\times10^{-3}\exp(-40{,}000/RT)\,\text{mole sec}^{-1}\text{ cm}^{-2}\text{ atm}$$

The fit of the data is not good at values of $CO/NO < 1$. In fact for pure NO the above simple model does not predict a first-order dependence of NO. Clearly a more sophisticated model is needed to explain the experimental findings.

Furusawa et al.[248] and Tsujimura et al.,[260,261] found that the rate of the catalyzed reduction of NO by CO was significantly faster than the rate of char-consuming reduction of NO, and under the condition [CO]/[NO]>>1, catalyzed reduction of NO by CO was the dominant mechanis. Their observation agreed with the mechanism for catalyzed reduction of NO by CO expressed by reactions (2-2.2) and (2-2.3).

(2). Catalytic Reduction of NO by CO over Calcined Limestone

The importance of calcined lime in NO_x reduction has been pointed out by Morikawa et al.[262]. Tsujimura et al.[260,261] measured the rate of NO reduction by CO over calcined limestone for a temperature range of 858-1195K in a fixed bed flow reactor. They used two types of limestone, Iwato and Buko, which contain 55.43% and 54.8% CaO, respectively. They evaluated the rate by assuming the reaction scheme

$$NO + CO \rightarrow CO_2 + 1/2N_2 \qquad (2\text{-}2.1)$$

which is catalyzed over the surface of calcined lime. Their experiments verified that the reaction was first-order with respect to both nitric oxide and carbon monoxide, and Arrhenius expressions were obtained as follows:

$$k_{2\text{-}2.1} = 3.41\times10^{7}\exp(-2.11\times10^{4}/T)\ \mathrm{ppm}^{-1}\ \mathrm{sec}^{-1}$$

from 858 to 943K, and

$$k_{2-2.1} = 1.56\text{x}10^2\exp(-8.92\text{x}10^3/T)\ \text{ppm}^{-1}\ \text{sec}^{-1}$$

from 943 to 1195K. These rate data indicate that calcined limestone has a high catalytic activity for NO reduction by carbon monoxide and the rate exceeds the rate of catalytic as well as non-catalytic NO reduction by char. However, the relative importance of the catalytic surfaces of limestone and char for NO reduction within the fluidized-bed combustor depends not only on the catalytic activity of these surfaces, but also on the available surface areas. The surface area is controlled by the concentrations of both the char and limestones and the extent of calcination and sulphur retention of the limestone. Thus an extensive investigation must be carried out to elucidate the relative importance of these two catalytic surfaces on NO reduction.

The observed activation energy of NO reduction by CO over calcined limestone by Tsujimura et al.[260,261] decreased over the temperature range 993-1195K. This phenomenon can be explained if two successive reactions participate in NO_x reduction. However, no change of product distribution above this temperature has yet been observed and the existence of an intermediate product could not be detected in the experiments of Tsujimura et al.

(3). Catalytic Reduction of NO by CO on Quartz Surfaces

Although quartz sand is often used as bed material for fluidized combustion of coal, it has been dismissed as a potential catalyzing material[248-250]. However, experiments made by Wittler et al.,[263] with $NO/CO/N_2$ mixtures in a quartz flow tube clearly showed that a quartz surface catalyzed the reduction of NO by CO if the mole fraction of CO was > 1%. They suggested that the short residence time employed by Furusawa et al.[248-250] was the reason they could find no reaction on quartz sand. To the present, no further investigations of the reduction of NO by CO on quartz have been reported.

(4). Catalytic Reduction of NO by CO on Metal Surfaces

Numerous metals, especially the noble metals such as Pt, Pd, Rh, and Ru are widely used as automotive exhaust catalysts. Of these precious metals, Rh is used in so-called three-way catalysts for simultaneous reduction of the concentrations of nitric oxide, carbon monoxide, and hydrocarbons in automobile exhaust.

The reaction of NO with CO catalyzed by various metal catalysts has been investigated intensely[264-291]. Kobylinski and Taylor's[265] study of the reduction of NO with CO and H_2 indicated that the catalytic activity decreased along the series Ru > Rh > Pt > Pd. They found that CO strongly inhibits NO reduction over Pt and Pd but to a lesser extent over Rh. Over Ru the presence of CO accelerated the reduction reaction. Reduction of NO in the presence of Pt and Pd produced NH_3 as the major product of the reaction of NO with H_2. Rh and Ru catalysts were found to be selective in the formation of N_2. N_2 was observed to be the major product of the reaction of NO with CO. In studies of NO reduction by CO over noble-metal catalysts under cycled feedstream conditions, Muraki and Fujitanl[279] observed that the catalytic activity followed the order Rh > Ru > Ir > Pd > Pt. They also observed that the activities of Pt and Pd catalysts increased when the feedstream was cycled.

Unland[287] reported from infrared studies of the reaction of NO and CO over noble-metal catalysts the observation of an intense band due to the isocyanate group, -NCO. He further showed that the intensity of these bands correlate with the propensity of these metals to form ammonia during NO reduction in hydrogen-containing systems. They proposed that these isocyanate species are adsorbed on the active metal and serve as intermediates in the reaction of NO and CO in the presence of H_2O to form ammonia. Betta and Shelef[266] have studied a number of different catalysts, in particular Pt and Ru supported on alumina, and have also observed intense infrared bands due to isocyanate but they found that most of the isocyanate is adsorbed on the alumina surface and not on the noble metal.

By contrast, the work of Voorhoeve and Trimble[269] and Solymosi et al.[288] clearly demonstrates that NCO is formed on the noble metal surfaces. Lorimer and Bell[270] also found intense infrared bands corresponding to CO chemisorbed on Pt with NCO and CN groups attached to the support as Si-NCO and Si-CN. They also found that the CO and NCO bands were more intense when [CO]/[NO] > 1 than when [CO]/[NO] < 1. They explained the adsorption of NCO on the support materials by the assumption that nascent NCO groups which formed on noble metal surfaces do not remain on the surface but migrate rapidly to the support where they are stabilized as M-NCO (where M represents the support material). Lorimer and Bell[270] also found that the rate of NO consumption through the formation of the NCO group was never greater than 10% and usually less than 5% of the rate of total NO consumption. They further observed that surface coverage of the noble metal by the NCO group was negligible and, hence, does not affect the availability of sites for either NO or CO adsorption.

Butler and Davis[267] have studied the kinetics of the reaction between CO and NO over alumina-supported Pd and Ru in a closed system by monitoring gas composition mass spectrometrically. Over the Pd catalyst the reaction may be represented by

$$d(P_{CO2})/dt = 0.3x10^{-17} \exp(-91.26\pm19 KJmol^{-1}/RT) P_{NO}{}^{2}/P_{CO}$$

(in units of mole cm^{-2} sec^{-1}) over a temperature range of 573-723K with P_{CO}/P_{NO} between 1 and 1.6. Over the Ru catalyst the rate is given by

$$d(P_{CO2})/dt = 1.09 \times 10^{-15} \exp(-82.4 \pm 15 KJmol^{-1}/RT) P_{NO}{}^0 P_{CO}{}^0$$

(in units of mole cm^{-2} sec^{-1}) over a temperature range of 523-623K with P_{CO}/P_{NO} between 1 and 5. These results are consistent with those of Kobylinski and Taylor[265] who also observed that the reduction of NO by CO over Pd was inhibited by CO.

The IR study of Eischens et al.,[289] on Pd-CO surface interactions, together with the later work by Palazov et al.[290] has established that CO is readily adsorbed by Pd. Adsorption of NO by Pd, on the other hand, also occurs but NO is more weakly adsorbed than CO.[287] This evidence indicates that when an excess of CO is present, the Pd surface is largely covered by CO.

From their observation of the second-order dependence on P_{NO}, Butler and Davis[267] suggested two possible mechanisms. In one case they proposed that two NO molecules associate with one adsorption site i.e., NO being adsorbed as a dimer as in (2-2.6).

$$2NO + S \dashrightarrow S\text{-}(NO)_2 \qquad (2\text{-}2.6)$$

This mechanism would be unlikely at catalytic temperatures. As another, more reasonable route, they suggested a rapid reaction between adjacently adsorbed molecules of CO and NO to give carbon dioxide and an adsorbed nitrogen atom as shown in (2-2.7) and (2-2.8),

$$CO_s + NO_s \text{-->} CO_{2s} + N_s \qquad (2\text{-}2.7)$$

$$CO_{2s} \text{-->} S + CO_2 \qquad (2\text{-}2.8)$$

followed by rapid reaction of the adsorbed nitrogen atom with another molecule of NO as in (2-2.9).

$$N_s + NO \text{-->} N_2O_s \qquad (2\text{-}2.9)$$

The adsorbed N_2O will react with an adjacently adsorbed CO to produce carbon dioxide and nitrogen according to (2-2.10)

$$N_2O_s + CO_s \text{-->} N_2 + CO_2 + 2S \qquad (2\text{-}2.10)$$

or desorb from the surface as N_2O.

However, in the study of reduction of NO by CO over Pt catalysts, Lorimer and Bell[270] proposed a dissociative adsorption mechanism as follows:

$$CO + S \text{-->} CO_s \qquad (2\text{-}2.11)$$

$$NO + S \text{-->} NO_s \qquad (2\text{-}2.12)$$

$$NO_s + S \text{-->} N_s + O_s \qquad (2\text{-}2.13)$$

$N_s + N_s \text{ --> } N_2 + 2S$ (2-2.14)

$N_s + NO_s \text{ --> } N_2O + 2S$ (2-2.15a)

$N_s + NO \text{ --> } N_2O + S$ (2-2.15b)

$CO + O_s \text{ --> } CO_2 + S$ (2-2.16)

where (2-2.11) and (2-2.12) represent the reversible chemisorption of NO and CO, respectively. In this scheme, the dissociation of NO is taken to occur via molecularly adsorbed NO as suggested by Lambert and Comrie[292] and Pirug and Bouzel[293]. Nitrogen formation is explained by the recombination of adsorbed nitrogen atoms. The work of Wilf and Dawson,[294] Schwaha and Bechtold[295] and Lambert and Comrie[292] presented experimental evidence for this mechanism. Lambert and Comrie[292] and Pirug and Bouzel[293] have also indicated that N_2O is formed by reaction (2-2.15a). The inclusion of reaction (2-2.15b) is based on the theoretical work of Weinberg and Merrill[296], which suggested that at moderate partial pressures of NO, reaction (2-2.15b) should be favoured over reaction (2-2.10a). The final step, reaction (2-2.16) described the removal of adsorbed oxygen from the surface. Lorimer and Comrie[292]pointed out that the rate-determining step was dissociation of NO as in reaction (2-2.13).

In their study of NO reduction by CO on Ru, Rh, Pd, and Ag[297] and Pd,[281] Bodanchikova et al.[297] and Pyatnitskii et al.[281] suggested a mechanism similar to that of Lorimer and Bell.[270] However, in Pyatnitskii et al.'s[281] mechanisms the reaction between two adsorbed oxygen atoms (2-2.17) and the reaction between adsorbed CO and adsorbed O atom (2-2.18),

$$O_s + O_s \text{ --> } 2S + O_2 \qquad (2\text{-}2.17)$$

$$CO_s + O_s \text{ --> } 2S + CO_2 \qquad (2\text{-}2.18)$$

were included since CO is easily adsorbed on palladium and is capable of reacting in the adsorbed state with adsorbed oxygen atoms. They also explained the accelerating influence of oxygen and the inhibiting influence of CO on the rate of the CO + NO reaction over Pd[265] by numerical calculation based on the their mechanism. More recently, Pyatnitskii et al.[283] improved the above mechanism by the addition of an N_2O decomposition reaction on the catalyst surface, i.e.,

$$N_2O + \text{surface} \text{ --> } O_s + N_2 \qquad (2\text{-}2.19)$$

and the conditions necessary to explain acceleration of the CO + NO reaction by oxygen were obtained.

By using the above mechanism, Pyatnitskii et al.,[281] demonstrated the existence of a multiplicity of stationary states and critical transitions in the CO + NO system over the Pd catalyst. They pointed out that the multiplicity of stationary states and the critical transitions were due to reaction (2-2.13).

More recently, the presence of multiple steady states and oscillations in the CO/NO reaction on Pt and Pd catalysts was observed and investigated by Schwartz and Schmidt[282] and Schuth and Wicke[284].

In Ru and Rh catalysts, both CO and NO are considered to be strongly adsorbed on the catalyst surface. Kobayashi and Shirasaki[298] reported that at 550K, the predominant form of NO adsorbed on Ru is molecular while at 650K or above dissociative adsorption occurs. From the results of Butler and Davis[267], it appears that NO is more strongly adsorbed than CO. For reaction mixtures with a CO/NO ratio as high as 5/1, a zero and a fractional order was obtained for p_{NO} and p_{CO}, respectively[267].

Dubois et al.[273] investigated the reduction of NO by CO on a Rh surface by using high-resolution electron energy loss spectroscopy (ELS). Their measurements indicate that both NO and CO associatively adsorb on a Rh(331) single-crystal surface at 300K. Chemisorbed NO readily dissociates on the surface upon heating to 450K. At 700K only oxygen is present on the catalyst surface. They also found that the addition of CO to this surface oxygen at 700K results in the formation of gaseous CO_2 and the removal of the adsorbed oxygen. They proposed a simple mechanism for the reduction of NO by CO to form N_2 and CO_2 as

$$2NO \dashrightarrow N_2 + 2O_s \qquad (2\text{-}2.20)$$

which is a combination of reactions (2-2.12), (2-2.13) and (2-2.14), and

$$2O_s + 2CO \rightarrow 2CO_2 \qquad (2\text{-}2.21)$$

which is the same as reaction (2-2.16).

Hecker and Bell[274] investigated the reduction of NO by CO over silica-supported Rh by an in situ infrared technique. They observed that the kinetics of the reduction of NO is positive order in CO but inverse order in NO and the dominant species presented on the surface during the reduction of NO by CO was CO. Their observation of an infrared band at 2040 cm^{-1} provided evidence of the existence of adsorbed CO on the surface. Temperature-programmed desorption studies[299-301] carried out with both supported and unsupported Rh have shown, that at elevated temperatures, adsorbed NO readily undergoes dissociation to form N and O atoms. Chin and Bell[302] estimated the activation energy for this process to be about 8 kcal/mol. Based on this estimation, Hecker and Bell[274] proposed a mechanism which is similar to that of Lorimer and Bell[270]. The major differences between the two mechanisms are that Hecker and Bell's mechanism proposes the formation of N_2 by reaction (2-2.22)

$$NO_s + N_s \rightarrow N_2 + O_s + S \qquad (2\text{-}2.22)$$

rather than reaction (2.14), and that the removal of adsorbed oxygen was through the reaction with adsorbed CO, i.e., (2-2.18) rather than (2-2.16). Reaction (2-2.14) has a higher activation energy than that for reaction (2-2.20).[299] Campbell et al.,[300] have shown that (2-2.18) occurs much more rapidly than reaction (2-2.16). Hecker and Bell also assumed that the rate-limiting step was dissociation of NO, i.e., reaction (2-2.13).

Root and Schmidt[277] studied nitric oxide reduction by CO on Rh(111) with temperature programmed reaction (TPR). They pointed out that the rate-determining step is reaction (2-2.13) rather than NO dissociation, and that the repulsive interactions between adsorbed CO and adsorbed nitrogen atoms lead to desorption of CO as a peak at 415K which is in the temperature range where reaction (2-2.13) occurs. Thus the extent of reaction of CO_s with NO_s is less than that between CO_s and O_s due to the lower coverage of CO caused by adsorbed N atoms and NO.

Jenkins and Voisey[264] examined the kinetics of catalyzed reactions of carbon monoxide with nitric oxide and/or oxygen on a steel surface. They found that the reaction of CO with NO was first order in [CO]. The proposed mechanism for catalyzed reduction of NO by CO on steel surfaces includes the associated adsorption of NO and CO, as in reactions (2-2.11) and (2-2.12), followed by reactions (2-2.33) and (2-2.24)

$$NO_s + CO_s \rightarrow M\text{-}N_s + S + CO_2 \qquad (2\text{-}2.23)$$

$$2N_s \rightarrow N_2 + 2S \qquad (2\text{-}2.24)$$

and the formation of N_2O through reaction (2-2.25).

$$N_s + NO \rightarrow N_2O + S \qquad (2\text{-}2.25)$$

By using this mechanism, they obtained the best fit of the calculated results with their experimental data.

As mentioned above, N_2O forms in significant amounts in the reduction of NO by CO over metal catalysts. Such catalysts have been used widely as three-way catalysts for simultaneous destruction of NO, CO and hydrocarbon in automobile exhaust. In recent years, the worries about the deleterious effect of N_2O emission, have prompted further examinations of the formation of N_2O in the reduction of NO by CO, and further work is needed.

According to Campbell[300], the path for N_2O formation in the reduction of NO by CO on catalyst surfaces is more likely to be reaction (2-2.15a)

$$N_s + NO_s \rightarrow N_2O + 2\text{Surface Sites} \qquad (2\text{-}2.15a)$$

rather than reaction (2-2.15b).

$$N_s + NO \dashrightarrow N_2O + S \quad (2\text{-}2.15b)$$

In the global form, the reduction of NO by CO can be expressed as follows[279],

$$2NO + 2CO \dashrightarrow N_2 + 2CO_2 \quad (2\text{-}2.26)$$

$$2NO + CO \dashrightarrow N_2O + CO_2 \quad (2\text{-}2.27)$$

If the ratio NO consumed/CO consumed ≈ 1, reaction (2-2.26) is predominant and N_2 is the primary product. On the other hand, if NO consumed/CO consumed ≈ 2, reaction (2-2.27) is predominant and N_2O will be the primary product. Catalyst selectivity for N_2O formation is given by the following expression.

$$\begin{aligned} Y_{N2O} &= N_2O_{formed}/(N_2O_{formed} + N_{2formed}) \\ &= 2(NO_{consumed} - CO_{consumed})/(NO_{consumed}) \end{aligned}$$

Hecker and Bell[274] investigated the effects of temperature on the selectivity for production of N_2O in the reduction of NO by CO over silica-supported Rh. They concluded that as the temperature increased from 463 to 498K, the selectivity increased slightly (76% to 81%). When the temperature is increased from 498 to 501K, the selectivity for N_2O formation suddenly decreased to about 70%, while the selectivity for N_2 formation suddenly increased to about 30%. Increasing the temperature above 501K results in a further decrease in N_2O formation and a corresponding increase in N_2

formation. They also observed that variation of the contact time over a sevenfold range had no effect on the distribution between N_2O and N_2 formation. This observation suggests that N_2O, once formed, does not undergo further reduction in the temperature range 453-533K. Hecker and Bell[268] also concluded that the overall activation energy for the formation of N_2O is the same as that for NO reduction resulting in N_2 formation. Based on their proposed mechanism, the overall rates of N_2O and N_2 formation are given by,

$$k_{N2O} = 0.5k_{NO}k_{2.15a} / (k_{2.15a} + k_{2.22})$$

$$k_{N2} = 0.5k_{NO}k_{2.22} / (k_{2.15} + k_{2.22)}$$

where k_{NO} is the overall rate of NO reduction.

Muraki et al.[280] investigated the kinetics of N_2O formation in the reduction of NO by CO over alumina-supported Pd catalysts. They found that the selectivity for N_2O formation increases with increasing temperature up to 673K and the maximum value of selectivity for N_2O formation is ≈ 65% at 673K. After 673K the selectivity for N_2O formation decreases with further increase in temperature. Their results also indicated that a variation of the contact time over a 17-fold range had no effect on N_2O selectivity confirming that once N_2O is formed it does not undergo further dissociation. Muraki et al. also examined the effects of the partial pressures of NO and CO on the reaction products. They found that as the temperature increased between 723 and 773K, the selectivity for N_2O formation suddenly decreased at S = [NO]/[CO] = 1.0, while at lower temperatures (623 and 673K), the selectivities for N_2O formation were almost constant (65%) at every value of S.

In order to clearly determine the product distribution in the NO/CO reaction, Muraki et al.[280] carried out a series of pulse reactions at various temperatures. They found that in the first pulse, N_2 formation increased with increasing temperature, while N_2O formation slightly decreased with increasing temperature. Further, the amount of N_2O formed was much less than the amount of N_2 formed. They also found that the amount of N_2 formed in the second pulse decreased and the amount of N_2O formed increased. The amount of N_2O formed after the second pulse decreased with further pulses. These results indicated that the N_2 formation on the reduced Pd surface was more efficient than on a slightly oxidized surface. However, N_2O formation on a slightly oxidized Pd surface was much more pronounced than on a reduced Pd surface.

In another paper, Muraki and Fujitanl[279] compared the selectivities of Rh, Ru, Pd, Ir and Pt catalysts. They concluded that as temperature increased, selectivity towards N_2O formation decreased for all catalysts except for Rh. In the case of the Rh catalyst, the selectivity for N_2O formation, Y_{N2O}, increased until 548K and then decreased with further increase in temperature. Selectivity for N_2O formation decreased in the order Pt > Pd > Ir

= Ru > Rh.

More recently, Cho et al.[303] studied the kinetics of the reduction of NO by CO over Rh/Al_2O_3 and Rh/CeO_2 using a packed-bed reactor and an isotopic reactant, ^{13}CO. They found that the amount of N_2O formed in the reaction increased with increasing temperature from 400K to 550K and that the temperature for maximum N_2O formation corresponds to the reaction lightoff temperature of the NO reduction. This suggested that the formation of N_2O may play an important role in initiating the CO + NO reaction. Based on this assumption, they proposed another pathway for N_2O formation as in reaction (2-2.28)

$$2NO_s \dashrightarrow N_2O + O_s + S \qquad (2\text{-}2.28).$$

They suggested that the adsorbed oxygen helped to initiate the surface reaction between CO_s and O_s, i.e. reaction (2.18).

2-3. CATALYTIC REACTION OF NO WITH H_2

The catalytic NO reduction by hydrogen over char and calcined limestone surfaces plays a significant role in fluidized bed combustion[304]. However, only one research group investigated this reaction and the results have been reported in two papers[250,261].

Furusawa et al.[250] reported the results of the investigation of the reduction of NO by H_2 over char surfaces at temperatures from 853 to 1173K. They found that the addition of hydrogen reduced the consumption of carbon almost to zero indicating that the surface catalyzed reduction of NO controlled overall NO destruction. They also found the major products to be nitrogen and ammonia. They provided the following expression for the relationship between the reactant and product concentrations.

$$[NO]_{consumed} = 2[N_2]_{produced} + [NH_3]_{produced}$$

From this relationship they proposed that the reactions (2-3.1) and (2-3.2) took place simultaneously over the char surface.

$$NO + H_2 \dashrightarrow H_2O + 1/2N_2 \qquad (2\text{-}3.1)$$

$$NO + 5/2H_2 \dashrightarrow NH_3 + H_2O \qquad (2\text{-}3.2)$$

Furusawa et al.,[250] measured the ratio $[NH_3]_{formed}/[NO]_{consumed}$ by changing the residence time at a constant reaction temperature.

They found that this ratio was constant at each temperature and decreased with increasing temperature. This result indicated that nitric oxide was primarily reduced to both ammonia and nitrogen and that secondary decomposition of ammonia could be assumed to be negligible. They also measured the rate of reduction of NO by H_2 on char surfaces and found that the overall rate was first order with respect to both [NO] and $[H_2]$. The Arrhenius expression was given as

$$k = 4.6 \times 10^9 T\exp(-12120/T) \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}.$$

They found that the rate obtained for a = 4 to 7 was approximately equal to the rate of noncatalytic reduction of NO by char, while at values of a = 91.6 to 96 the rate of NO reduction was drastically increased. (a is the ratio of H_2 concentration to NO concentration at the inlet of the reactor). This result indicated that an excess of hydrogen might play an important role in controlling NO_x emission of a fluidized bed combustor operated with staged air firing.

Tsujimura et al.[261] also investigated the reduction of NO by H_2 over calcined limestone over the temperature range 850-1103K. They found that the major products were N_2 and NH_3 and that the molar relationship between N_2 and NH_3 suggested that reactions (2-3.1) and (2-3.2) also occurred over calcined limestone. The ratio $[NH_3]_{formed}/[NO]_{consumed}$ was constant at each temperature and decreased with increasing temperature as in the case of a char surface. This indicated that similar to the situation of a char surface, the reduction of NO by H_2 on calcined limestone was primarily to NH_3 and N_2 and that the secondary decomposition of NH_3 could be neglected. They also found that the rate expression was first order with respect to [NO] and [H_2]. They obtained an Arrhenius expression for the rate constant for the overall reduction of NO by H_2 over calcined limestone as

$$k = 7.0\text{x}10^{19} \exp(-9320/T) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

They pointed out that the rate of NO reduction by H_2 over such a catalytic surface was as large as the rate observed for NO reduction by CO on a similar surface.

Johnson[304] suggested that the catalytic effects of char and CaO are very important for fuel-N conversion in FBC. CO, H_2 and char are important reactants for NO reduction, while volatile fuel-N has only a minor influence on the production of NO_x species.

Reliable kinetic information about these catalytic reactions is not sufficiently developed to make further predictions on the emission of NO and N_2O from FBC possible. Further study is needed.

2-4. REDUCTION OF NO BY NH_3

(1). Thermal $DeNO_x$ Process -- The Homogeneous NH_3-NO-O_2 Reaction

The investigation of the homogeneous reaction of NO with NH_3 was first studied by Lyon[305] and Lyon and Benn[306]. Their study was initiated in an attempt to find a noncatalytic selective mechanism to reduce NO emission in combustion processes, and is often referred to as the Thermal $DeNO_x$ process. Lyon[307] published a review on the Thermal $DeNO_x$ process in 1987, and in this review, the kinetics and mechanism, injection system design, application to coal firing, costs, and commercial status were discussed. In this report, we concentrate our attention on the kinetics and mechanism of the process and the possibility of the formation of N_2O in the process.

In the initial report of the discovery of the NH_3-NO-O_2 system, Lyon[305] reported that with O_2 present, a nearly quantitative reduction of NO by NH_3 could be obtained at 1255K, and that when no O_2 is present, NO removal is trivial. It should be noted that no reaction was detected between NH_3 and O_2 at this temperature. Another set of experiments reported in this paper indicated that in the absence of NH_3 the reaction of NO and O_2 to form NO_2 is too slow to be observable. Lyon also reported that the main products of the reaction of the NH_3-O_2-NO system were N_2 and water. They determined that for every mole of NO which disappeared, 0.02 mole of N_2O

appeared in the product gases.

Another interesting result obtained by Lyon[306] was that the reduction of NO by NH_3 occurred only in a narrow temperature range centred at T = 1250K. At lower temperatures, the reaction is so slow as to be negligible, while at higher temperatures, NH_3 tended to oxidize to form NO. If a small amount of H_2 was mixed with the NH_3, the temperature for optimum NO reduction decreased, and the extent of decrease grew with the amount of H_2 added.

In a subsequent publication, Lyon and Benn[306] reported that over the temperature range 1145-1227K, in which the concurrent oxidation of NH_3 to form NO was a minor process, the reduction of NO obeyed the simple rate law.

$$d(\ln[NO])/dt = -k_R\ [O_2]^{1/2}\ [NH_3]^{1/2}\ [He]^{-1}$$

where $k_R = 1.8\times10^{12} \exp(-46500/RT)\ \mathrm{sec}^{-1}$. The above expression describes the rate of the reduction over the pressure range 1.07 to 2.14 atm and for the reactants in such relative proportions that $[He]>>[O_2]>>[NH_3]>>[NO]$. They also found that if $[NH_3]$ was increased so that $[NH_3]$ approached $[O_2]$, the extent of NO reduction occurring during a given reaction time could decrease from a nearly quantitative reduction to little or no reduction and that the concentration needed to cause this self-inhibiting effect was found to increase with increasing $[O_2]$, increasing reduction time, and increasing temperature.

In his initial report of the NH_3-NO-O_2 reaction, Lyon[305] proposed a simple chain mechanism for the reaction as follows:

$$NH_3,\ O_2 \dashrightarrow \text{free radicals} \tag{2-4.1}$$
$$NH_2 + NO \dashrightarrow N_2 + H + OH \tag{2-4.2}$$
$$NH_2 + NO \dashrightarrow N_2 + H_2O \tag{2-4.3}$$
$$H + O_2 \dashrightarrow OH + O \tag{2-4.4}$$
$$O + NH_3 \dashrightarrow OH + NH_2 \tag{2-4.5}$$
$$OH + NH_3 \dashrightarrow H_2O + NH_2 \tag{2-4.6}$$
$$N + NH_3 \dashrightarrow H + NH_2 \tag{2-4.7}$$

In this mechanism, NH_2 radicals produced in (2-4.1) react with NO by one of two channels, (2-4.2) and (2-4.3). Subsequent reactions (2-4.4), (2-4.5), (2-4.6), and (2-4.7) regenerate the NH_2 radicals. They pointed out that if the reaction of NO occurs by channel (2-4.2) one quarter to one half of the time, a self-sustaining chain reaction is possible for the three-component mixture $NH_3/NO/O_2$.

Lyon and Benn[306] further developed the above mechanism by adding the following reactions for chain termination,

$$2NH_2 + He \dashrightarrow N_2H_4 + He \tag{2-4.8}$$
$$N_2H_4 \dashrightarrow \text{Stable Products} \tag{2-4.9}$$

and self inhibition.

$$H + NH_2 \text{ --> } H_2 + NH_2 \qquad (2\text{-}4.10)$$

$$H_2 + O \text{ --> } OH + H \qquad (2\text{-}4.11)$$

$$H_2 + OH \text{ --> } H_2O + H \qquad (2\text{-}4.12)$$

By using this mechanism, Lyon and Benn explained why NH_3-NO-O_2 mixtures undergo a rapid chain branching reaction while NH_3-NO and NH_3-O_2 mixtures do not react. Their mechanism also accounted for the reaction order and the self inhibition effect. However, because this mechanism did not include the reaction steps by which the concurrent oxidation of NH_3 to NO takes place, it did not explain the sensitivity of the reaction to temperature and the influence of addition of H_2 on the temperature "window". Further, many reactions which might be of importance have not been considered, and chain initiation and three body termination are left largely undefined.

The kinetics and mechanism of the Thermal $DeNO_x$ process also has been investigated by various other authors[308-328]. Salimian and Hanson[308] recognized that the reaction of NH_2 with NO does not produce N_2, OH, and H directly as predicted in reaction (2-4.2). Instead, this channel yields OH and N_2H, as shown in reaction (2-4.13).

$$NH_2 + NO \text{ --> } OH + N_2H \qquad (2\text{-}4.13)$$

followed by dissociation of N_2H to N_2 and H. They also investigated the use of model additive mixtures such as NH_3/CO, and NH_3/H_2O_2, which have been shown to promote removal of NO above 825K. These additives are attractive because of their low cost and the potential effectiveness at temperatures below 1200K.

Miller et al.[309] developed a more comprehensive mechanism, which included 82 elementary reactions and characterized more accurately the main features of the $DeNO_x$ process. They assumed that the production of NH_2 was mainly due to the reaction of NH_3 with OH, O and H radicals as in reactions (2-4.14), (2-4.15) and (2-4.16).

$$NH_3 + OH \dashrightarrow NH_2 + H_2O \qquad (2\text{-}4.14)$$

$$NH_3 + O \dashrightarrow HNO + H \qquad (2\text{-}4.15)$$

$$NH_3 + H \dashrightarrow NH_2 + H_2 \qquad (2\text{-}4.16)$$

They examined possible pathways for the reaction of NH_2 with NO and concluded that all the reactions (2-4.2), (2-4.13) and (2-4.17) could occur at high temperature, while reactions (2-4.2) and (2-4.13) could be important at low temperature.

$$NH_2 + NO \dashrightarrow N_2OH + H \qquad (2\text{-}4.17)$$

and that the product N_2OH could dissociate to form N_2O,

$$N_2OH + H \text{ --> } N_2O + H_2 \qquad (2\text{-}4.18)$$

$$N_2OH + O \text{ --> } N_2O + OH \qquad (2\text{-}4.19)$$

$$N_2OH + OH \text{ --> } N_2O + H_2O \qquad (2\text{-}4.20)$$

They assumed that the product N_2H of reaction (2-4.13) could react with NO to form N_2 and HNO as in 2-4.21.

$$N_2H + NO \text{ --> } N_2 + HNO \qquad (2\text{-}4.21)$$

They proposed that the concurrent oxidation of ammonia to form NO occurred through reaction (2-4.22)

$$NH_2 + OH \text{ --> } NH + H_2O \qquad (2\text{-}4.22)$$

and the NH that formed reacted with O_2 and OH to form HNO

$$NH + O_2 \text{ --> } HNO + O \qquad (2\text{-}4.23)$$

$$NH + OH \text{ --> } HNO + H. \qquad (2\text{-}4.24)$$

Finally, HNO dissociated or reacted with OH to form NO,

$$HNO + M \text{ --> } NO + H + M \qquad (2\text{-}4.25)$$

$$HNO + OH \text{ --> } NO + H_2O \qquad (2\text{-}4.26)$$

They explained the "temperature window" effect as follows: At temperatures below approximately 1000K, in the reaction sequence leading to NO reduction, the chain terminating steps dominate over the chain branching steps. These effects lead to a rate of NH_3 --> NH_2 conversion which is insufficient to produce any significant NO reduction on time scales of practical interest. In the temperature range 1000-1500K, the mix of branching and termination reactions is such that NH_3 --> NH_2 conversion is sufficiently rapid that the channels for NO reduction (2-4.17), (2-4.13) are dominant over the channel for NO formation (2-4.22). This results in a net decrease in the concentration of NO through formation of N_2. However, as temperature is increased above 1500K, the NO formation channel becomes dominant since chain branching processes become increasingly more important than termination steps. This causes a more rapid build up and generally higher levels of OH. Reaction (2-4.22) then begins to be competitive with (2-4.13) by 1250K and becomes dominant at 1500K.

They explained the influence of addition of H_2 on the NH_3-NO-O_2 system as resulting from a dramatic increase in OH concentration due to the following reactions,

$$OH + H_2 \longrightarrow H_2O + H \qquad (2\text{-}4.27)$$

$$H + O_2 \longrightarrow OH + O \qquad (2\text{-}4.28)$$

$$O + H_2O \longrightarrow OH + OH. \qquad (2\text{-}4.29)$$

This increase in [OH] allowed more rapid conversion of NH_3 to NH_2. However, because of this added OH the temperature, where the channel for NO formation becomes competitive with that for NO reduction, is lower. Consequently the temperature window for optimum reduction of NO formation is lower.

Miller et al.[309] also evaluated their model against flame data and found that their calculations were generally in reasonable agreement with lean flame experiments. However, they were not as successful in modelling rich flame experiments. They suggested that the discrepancies may be due to errors in the flame data.

Silver[310] extended the model to include the effects of SO_x on the efficiency of NO reduction. He found that in the presence of 1000 ppm SO_x, the optimal temperature for NO reduction was raised by 30-50K and that above this temperature the efficiency for NO removal was slightly improved. He explained the phenomenon on the basis that reaction (2-4.30) acts as a sink for oxygen atoms.

$$SO_2 + O \dashrightarrow SO_3 \qquad (2\text{-}4.30)$$

These atoms otherwise formed OH by reaction (2-4.29). By lowering the hydroxyl concentration, a shift of the temperature window to higher temperatures would be expected. Furthermore, reaction (2-4.31)

$$SO_3 + H \dashrightarrow SO_2 + OH \qquad (2\text{-}4.31)$$

ultimately resulted in a decrease in the concentration of OH, since in the absence of SO_3, each hydrogen atom can form up to three OH radicals by reactions (2-4.28) and (2-4.29). His results indicated that the use of sulfur-laden fuels should not hinder the performance of the Thermal $DeNO_x$ process, and in fact may somewhat increase the temperature range over which it is effective.

The mechanism originally proposed by Miller and coworkers was tested by Kimball-Linne and Hanson[311]. They used a combustion-driven flow reactor (CDFR), consisting of a laminar flat-flame burner, an ammonia injection section, and a plug-flow reactor section. Concentrations of NO, NH_3, OH, and reactor temperature were measured along the CDFR centerline, providing a Thermal $DeNO_x$ data base over the temperature range 1050K to 1450K, for ratios of $[NH_3]_{injected}/[NO]_{initial}$ from 1 to 3. They found that Miller's model yielded reasonable agreement with experimental data using a = 0.48 at 1050K, increasing a to > 0.8 at 1400K
$(a = k_{(2-4.13)}/(k_{(2-4.3)} + k_{(2-4.13)}))$ and with $k_{(2-4.22)} = 6.0\text{x}10^{12}$ mole/cm^3 s.

The model developed by Dean, Degregoria, Hardy, and Lyon (the DDHL model)[312] resembles qualitatively the models published by Miller et al.[309] The DDHL model also explains the temperature window as resulting from the two channels for reaction of NH_2. However, the reactions of NH_2 with O_2 (2-4.32) and O (2-4.33) have been added.

$$NH_2 + O_2 \rightarrow HNO + OH \qquad (2\text{-}4.32)$$

$$NH_2 + O \rightarrow NH + OH \qquad (2\text{-}4.33)$$

The products HNO and NH in (2-4.32) and (2-4.33) also form NO through (2-4.23), (2-4.25), (2-4.26) and reaction (2-4.34).

$$HNO + NH_2 \rightarrow NH_3 + NO \qquad (2\text{-}4.34)$$

The DDHL model also proposes quite different reactions for N_2H, eg., (2-4.35) and (2-4.36)

$$N_2H + NH_2 \rightarrow NH_3 + N_2 \qquad (2\text{-}4.35)$$

$$N_2H + M \rightarrow N_2 + H \qquad (2\text{-}4.36)$$

from that in Miller's model, i.e., reaction (2-4.18).

Although several complete computer models for the Thermal-DeNO$_x$ system have been developed, there are several rate constants which remain unknown or are in some doubt. Among those reactions with doubtful rate parameters, perhaps the most important which warrant further investigation are reactions (2-4.22), (2-4.26) and (2-4.36).

(2). Catalytic Reduction of NO by NH_3 over Activated Carbon

Interest in the catalytic reduction of NO by NH_3 was stimulated by the possibility of simultaneous removal of SO_x and NO_x from waste gas[329]. The catalytic reaction of NO with NH_3 in an oxygen-free system was proposed by Wong and Nobe[330,331] and Nam[332] to proceed according to reaction (2-4.37),

$$6NO + 4NH_3 \xrightarrow{Surface} 5N_2 + 6H_2O \qquad (2\text{-}4.37)$$

and in the presence of excess O_2 by reaction (2-4.38).

$$4NO + O_2 + 4NH_3 \xrightarrow{Surface} 4N_2 + 6H_2O \qquad (2\text{-}4.38)$$

The catalytic reduction of NO by NH_3 over metals[333], metal oxides such as V_2O_5, Cr_2O_3, Fe_2O_3, etc., [334-347] zeolite crystals[348,349], and hydrogen mordenite[350] has been investigated extensively, and some intensive literature reviews[330,348] have been published. In this report, we will review the works on other catalysts.

Mochida et al.[351] reported that activation of coke by the impregnation of sulphuric acid and subsequent heat treatment at 700K markedly enhanced its activity as a catalyst of reactions (2-4.37) and (2-4.38). With the coke activated by this method, the nitrogen yield after 90 min of reaction was as much as 70%, while for the original coke the yield of nitrogen after 90 min of reaction was only 10%. They also found that the activity decreased in repeated runs but that the activity could be restored by further heat treatment at 670K. They attributed the sevenfold increase in activity primarily to oxidized functional groups which formed on the coke surface by the sulphuric acid during its desorption. They also suggested that the increased surface area which resulted on heat treatment of the sulphuric acid treated coke might be a factor. They observed that the activity gradually decreased with repeated runs as a result of water adsorption.

Kusakabe et al.[352] reported that coke activated at 673K with 100 to 500% (weight %) sulphuric acid increased the rate of N_2 formation by a factor of 1.5 - 2.6 compared to the rate observed for the original catalyst. They also found that the rate of NO reduction was increased by the presence of oxygen but was retarded by water vapour. They obtained a rate expression for N_2 formation in NO reduction for the NH_3-NO-O_2 mixture over activated coke as follows,

$$r_{N2} = k_2 \exp(409/T) P_{NO}{}^{0.86} P_{O2}{}^{0.2} P_{NH3} / (1 + k_{NH3} P_{NH3} + k_{H2O} P_{H2O})$$

where:

$$k_{NH3} = (2.3\text{x}10^{-3}) \exp(1443/T) \ \text{Pa}^{-1}$$

$$k_{H2O} = (2.2\text{x}10^{-6}) \exp(2044/T) \ \text{Pa}^{-1}$$

The value of k_2 was found to be a function of the H_2SO_4 loading and was determined as $4.2\text{x}10^{-12}$ for the AC-300% catalyst. They found that when the coke was activated with a higher H_2SO_4 loading, the adsorption of NO decreases, while that of NH_3 increases. This indicates that adsorption sites of NO are different from those of NH_3. Mochida et al.[353] suggested the following schemes for the adsorption of NO and NH_3:

$$NO + O + Carbon \dashrightarrow NO_2\text{-Carbon} \qquad (2\text{-}4.39)$$

$$NH_3 + HO\text{-Carbon} \dashrightarrow NH_4O\text{-Carbon} \qquad (2\text{-}4.40)$$

Kuhl et al.[354] investigated the catalytic activity of different carbon catalysts for NO reduction with ammonia in the presence of oxygen and water vapour. Their catalysts were characterized by total surface area (TSA) and active surface area (ASA). The latter was determined by measuring the coverage of the surface with oxygen complexes upon exposure to O_2 at 573K for 24h. They obtained a linear relationship between catalytic NO reduction and ASA, at low-ASA values.

(3). Catalytic Reduction of NO by NH_3 over Char and Limestones

Interest in catalytic reduction of NO by NH_3 was stimulated by the fact that limestones were used as sorbents for sulfur dioxide in fluidized bed coal combustors and represented the majority of the solid bed. However, only one study on the effects of calcined limestone on the NH_3-NO-O_2 reaction has been reported by Lee et al. in two published papers[355,356].

Lee et al.[355] investigated the effect of calcined limestone in a packed bed reactor over the temperature range 1000-1100K and examined inlet concentrations of oxygen ranging from 0 to 5%, NH_3 from 0 to 1000 ppm, and NO from 0 to 1000 ppm, monitoring both NH_3 and NO decay as a function of reaction time.
They concluded that the calcined limestone had a catalytic effect on both NH_3-NO and NH_3-NO-O_2 reactions (2-4.37) and (2-4.38) as well as on NH_3-O_2 reaction. They found that the combined catalytic effect of calcined limestone in NO reduction from NH_3-NO and NH_3-NO-O_2 reactions and NO formation from NH_3-O_2 reaction, led to an increase in NO concentration in the outlet stream. This indicated that in the presence of calcined limestone, the NO formation in the NH_3-O_2 reaction was more dominant than the NO reduction in NH_3-NO and NH_3-NO-O_2 reactions.

In another paper, Lee et al.[356] reported the results of their investigation on the effects of sulfated limestone for the above reactions under the same conditions as used to study on the effects of calcined limestone. They found that the calcined limestone had a stronger catalytic effect than sulfated limestone in producing NO, while the catalytic effect for NO reduction from NH_3-NO and NH_3-NO-O_2 reactions was almost the same. So the sulfated limestone has an effect of decreasing NO outlet concentration.

More experimental data are needed to clarify the mechanism of the heterogeneously catalyzed reactions.

(4). Catalytic Reduction of NO by NH_3 over $CaSO_4$

The only study of the catalytic reduction of NO by NH_3 over a $CaSO_4$ surface was reported by Lee et al.[355]. They expressed the rate of reaction as

$$-r_{NO} = k\,[NO][NH_3]$$

with

$$k = 5.1\text{x}10^5\ m^3\ kmol^{-1}\ s^{-1}$$

at T = 1100K

They also found that the rate constant increased by a factor of 5 if oxygen is absent.

2-5. OXIDATION OF NH_3

(1). Homogeneous Oxidation of NH_3

Early investigations of the homogeneous oxidation of NH_3 have been carried out by Takeyama and Miyama[357-365], Bradley et al.[366], and Bull[367] in shock tubes, by Fenimore et al.[368], Nadler et al.[369], Kaskan and Hughes[370,371], and Andrews and Gray[372], Maclean and Wager[373] in flames, and by Husain and Norrish[374] using a flash photolysis technique. Since the 1970's, the study of the kinetics of ammonia oxidation has become important for the following reasons; i) to assist in clarifying the mechanism of formation of "fuel NO_x", ii) to contribute to a better understanding of the mechanism of Thermal-DeNO$_x$ process, and iii) to contribute to an understanding of the oxidation of ammonia to form nitrogen oxide in the troposphere and stratosphere, currently one of the most important problems of atmospheric chemistry.

Over the past twelve years, the oxidation of NH_3 has been investigated by Fujii et al.[375], and Salimian et al.[376] in shock tubes, by Dean et al.[312,328] in a flow tube, by Branch and Sawyer[327] in an arc-heated flow reactor, by Dean et al.[377], and Fisher[378] in flames, and by Pagsberg et al.[379] using pulse radiolysis.

The initial steps of the oxidation are generally accepted to be the production of NH_2 by reaction of NH_3 with O_2 and OH[361,366,367] as in reactions (2-5.1) and (2-5.2).

$$NH_3 + O_2 \dashrightarrow NH_2 + HO_2 \qquad (2\text{-}5.1)$$

$$NH_3 + M \dashrightarrow NH_2 + H + M \qquad (2\text{-}5.2)$$

There is, however, considerable disagreement as to the subsequent reactions in the oxidation of NH_3.

Husain and Norrish[374] studied NH_3 oxidation by flash photolysis at about 1500K and proposed a mechanism in which HNO was considered to be a degenerate branching agent,

$$NH_2 + O_2 \dashrightarrow HNO + OH \qquad (2\text{-}5.3)$$

$$NH_3 + OH \dashrightarrow NH_2 + H_2O \qquad (2\text{-}5.4)$$

and that NO was formed by the breakdown of HNO as in reaction (2-5.5).

$$HNO + M \dashrightarrow NO + H \qquad (2\text{-}5.5)$$

This mechanism was supported by the work of Bull[367] in shock tube studies in the temperature range 1500-4500K. He obtained an expression for the induction time related to the concentration of O_2 as follows:

$$\log[O_2]_t = -10.71 + [(30{,}500 \pm 4800)/RT] \text{ (mole sec l}^{-1}\text{)}.$$

Furthermore, Bull proposed reaction (2-5.6)

$$HNO + HNO \dashrightarrow N_2O + H_2O \qquad (2\text{-}5.6)$$

to explain his and Husain's observation of N_2O in the final products.

Bradley et al.[366] obtained the induction time for O_2 to be

$$\log[O_2]_t = -11.6 + (34{,}000/RT) \text{ (mole sec } l^{-1}).$$

The mechanism proposed by Bradley et al.[366] was similar to that of Bull, except that a pathway (reaction (2-5.7)) for the formation of NO from HNO was added.

$$HNO + O_2 \dashrightarrow [NO + HO_2] \dashrightarrow H + O_2 + NO \qquad (2\text{-}5.7)$$

They concluded that NH was not important in the oxidation of ammonia .

Branch and Sawyer[327] studied the over-all kinetics of the gas-phase oxidation of ammonia in an arc-heated flow reactor in the temperature range 1106-1377K. They found the main stable products to be water vapour and nitrogen with no NO, NO_2, or N_2O detected. They obtained a rate expression for the consumption of ammonia as follows,

$$-d[NH_3]/dt = k[NH_3]^{0.86\pm.08}[O_2]^{1.04\pm.13}$$

with

$$k = 4.9\text{x}10^{14} \exp[-(39{,}031 \pm 5{,}500)]/RT \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

However, the early work of Takeyama and Miyama[357,361] found that the rate of ammonia consumption immediately after the induction period could be expressed as

$$-(d[NH_3]/dt)_0 = k_0 \ [NH_3]^{1.5}[O_2]^{0.5}[Ar]^{0.5}$$

with

$$k_0 = 10^{12.77} \exp(-38{,}800/RT) \ 1^{1.5} \text{ mole}^{-1.5} \text{ sec}^{-1}.$$

They observed that [NH] reached a maximum value before [OH], and then decayed rapidly. They proposed a different mechanism for the reaction of NH_2 with O_2 as follows:

$$NH_2 + O_2 \text{ --> } NH + HO_2 \qquad (2\text{-}5.8)$$

$$NH + O_2 \text{ --> } NO + OH \qquad (2\text{-}5.9)$$

$$OH + NH_3 \text{ --> } NH_2 + H_2O \qquad (2\text{-}5.4)$$

$$HO_2 \text{ --> } OH + O \qquad (2\text{-}5.10)$$

$$O + NH_3 \text{ --> } OH + NH_2. \qquad (2\text{-}5.11)$$

Drummond[291] has supported this mechanism with his experimental results. Bull[367], however, pointed out that it is difficult in the application of this mechanism to visualize a side reaction which could account for the presence of N_2O in the system. Despite this problem, the reaction mechanism cannot be ruled out altogether since it includes participation of NH and HO_2 species.

Fujii et al.[375] considered 15 reactions which included their previous scheme, the Husain-Bull-Bradley mechanism and the well-known H_2-O_2 reactions. As a result of the comparison of calculations with experiment, they found that their previous scheme does not explain the experimental temperature dependence of the induction period and that the ammonia concentration curves calculated did not show the accelerating rate of NH_3 consumption observed. On the other hand, both the temperature dependence of the induction period and the profile of the ammonia consumption, calculated according to the Husain-Bull-Bradley scheme augmented by H_2-O_2 reactions reproduced the experimental results providing the appropriate values for the rate constant of reaction (2-5.3), were used. They concluded that this expanded scheme was more plausible and obtained a value for the rate constant of reaction (2-5.3) from the fit as follows,

$$k_{2\text{-}5.3} = 10^{12.5} \exp(-2.0 \text{ kcal/RT}) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

Furthermore, they suggested that the reaction (2-5.3) occurred through an intermediate species $(NH_2O_2)^*$ which was in equilibrium with reactants as in reaction (2-5.3a)

$$NH_2 + O_2 <--> (NH_2O_2)^* \qquad (2\text{-}5.3a)$$

or could undergo reaction as in reactions (2-5.3a1) and (2-5.3a2).

$$NH_2O_2^* \text{ --> } HNO + OH \qquad (2\text{-}5.3a1)$$

$$NH_2O_2^* \text{ --> } NH_2O_2 \qquad (2\text{-}5.3a2)$$

They obtained the rate constants for the forward (k_f) and reverse (k_r) steps of reaction (2-5.3a) and for reaction (2-5.3a1), (k_d), in the temperature range 1500-1800K as follows:

$$k_f = 10^{12.5} \exp(-15 \pm 5 \text{ kcal/RT}) \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

$$k_r = (1.0 \pm 0.3) \times 10^{10} \text{ sec}^{-1}$$

$$k_d = (1.3 \pm 0.3) \times 10^{10} \text{ sec}^{-1}.$$

The work of Dean et al.[312] in a flow tube over a temperature range of 1279-1323K showed that the rate of NH_3 oxidation was zero order in NH_3, increased with increasing $[O_2]$, was inhibited by the presence of H_2O, and promoted by the addition of H_2 or NO. They proposed a comprehensive mechanism which was similar to that of Miyama's but included a channel for NO reduction by NH_2.

More recently, Salimian et al.[376] used N_2O as a thermal source of O atoms to oxidize ammonia. In the NH_3-N_2O-Ar system, the rate limiting step is unimolecular decomposition of N_2O, a reaction whose rate constant is accurately known through numerous studies. This method avoided the complexities of the reaction of NH_2 with O_2 allowing the NH-O and NH-OH reactions, which lead to NO production, to be isolated from NH-O_2 reactions. A detailed kinetic model, which included 60 reactions of the N-O, N-H, N-H-O and C-H systems, was developed and successfully predicted their experimental results. Their mechanism indicated that reactions involving the HNO radical, which was primarily produced through the reaction of O atoms with NH_2, provided the major NO producing paths. The reactions of N and NH_2 with NO were the important NO removing steps, and under rich conditions, NH_i-NH_j (where i and j represent integers) interactions played a critical role in the fast removal of ammonia and production of N_2 through non-NO paths.

(2). Catalytic Oxidation of NH_3 over Char and Limestone

The oxidation of NH_3 over char and limestone plays an important role in the formation of NO in fluidized bed combustion[304]. There are two channels for the oxidation of NH_3 as shown in reactions (2-5.4) and (2-5.5).

$$NH_3 + 5/4O_2 \xrightarrow{Surface} NO + 3/2H_2O \qquad (2\text{-}5.4)$$

$$2NH_3 + 3/2O_2 \xrightarrow{Surface} N_2 + 3H_2O \qquad (2\text{-}5.5)$$

The only published work on the catalytic oxidation of NH_3 over char is that of Furusawa et al.[380]. They obtained the rate expression of NO production (reaction (2-5.4)) over char surfaces as

$$r_{NO} = k_{(2\text{-}5.4)}[NH_3][O_2],$$

and the rate coefficients $k_{(2\text{-}5.4)}$ as 10^{15} cm^3 mole^{-1} s^{-1} at 1073K and 5.9x10^{15} cm^3 mole^{-1} s^{-1} at 1100K. They also obtained a rate expression for reaction (2-4.5) over char as

$$-r_{NH3} = k_{(2\text{-}5.5)}[NH_3][O_2]$$

and the rate coefficient $k_{(2\text{-}5.5)}$ as 3.3x10^{15} cm^3 mole^{-1} s^{-1} at 973K.

The studies of oxidation of NH_3 over a limestone surface in fluidized bed combustion were reported by Furusawa et al.[380] and Lee et al.[355,356].

Furusawa et al.[380] obtained rate expressions for reactions (2-5.4) and (2-5.5) over calcined limestone as

$$r_{NO} = k_{(2\text{-}5.4)}[NH_3][O_2]$$
$$r_{NO} = k_{(2\text{-}5.5)}[NH_3][O_2]$$

respectively. They also obtained the value of the rate constant $k_{(2\text{-}5.4)}$ to be 2.4x10^{15} cm^3 mole^{-1} s^{-1} at 1073K and 3x10^{15} cm^3 mole^{-1} s^{-1} at 1100K and the value of $k_{(2\text{-}5.5)}$ to be 6x10^{14} cm^3 mole^{-1} s^{-1} at 1073K and 7.5x10^{14} cm^3 mole^{-1} s^{-1} at 1100K. They concluded that the rate of ammonia oxidation within the bed of calcined limestone was the most rapid among all the reactions involved in NO formation and destruction and that the selectivity of the nitric oxide formation was high over a range of temperature pertinent to fluidized bed combustion.

Lee et al. studied the oxidation of NH_3 over calcined limestones[355] and sulfated limestones[356]. They concluded that both calcined and sulfated limestones have a catalytic effect on NH_3 oxidation, increasing the rate of NO formation in the packed bed reactor and that the calcined limestone had a stronger catalytic effect than the sulfated limestone on NO formation.

2-6. DISSOCIATION OF NH_3

(1). Thermal Dissociation of NH_3

Little attention has been paid to the homogeneous decomposition of ammonia at high temperatures, mainly because of the fact that the heterogeneous reaction predominates under normal conditions.[381] Since the sixties, there have been several investigations of the thermal dissociation of NH_3, all carried out in shock tubes. The detection methods included IR emission of NH_3 at 2.7-3.2u[382-384], UV absorption of NH_3 at 220nm[381,385-387], UV absorption of NH at 336nm[384], and mass spectroscopy.[388-392]

Table 2-6.1. summaryes the published overall rate constants for the thermal decomposition of NH_3 and related reactions obtained in these studies.

It has been generally accepted that the primary and rate limiting step of the thermal dissociation of NH_3 is the unimolecular decomposition of NH_3[381,384],

$$NH_3 + M \text{ --> } NH_2 + H + M. \qquad (2\text{-}6.1)$$

Bradley et al.[384] detected NH by monitoring the emission from NH radicals and found that the NH concentration increased according to the following expression.

$$[NH] = k[NH_3]^2[Ar]t^2$$

They proposed a chain mechanism for the dissociation which included NH_2 as a chain carrier as shown in reactions (2-6.2) and (2-6.3).

$$NH_2 + NH_3 \dashrightarrow N_2H_3 \qquad (2\text{-}6.2)$$

$$N_2H_3 \dashrightarrow NH + NH_2 \qquad (2\text{-}6.3)$$

Table. 2-6.1. Summary of the Published Overall Rate Constants for Thermal Dissociation of Ammonia and for Some Related Reactions

Temperature	BGAS	Pressure	Rate expression	LOGA $cm^3 mole^{-1} s^{-1}$ or s^{-1}	E/R(T)	METHOD	REF
Overall reaction:							
2000-3000K	Ar	2-7torr	$-r[NH_3]=k[NH_3][Ar]$	15.6	41770	Shock Tube, IR Emission,UV Absor.	384
2000-3000K	Ar	1.21atm	$=k[NH_3]^{1.5}[Ar]^{0.5}$	15.39	39100	Shock Tube, IR Emission	383
2215-2750K	Ar	2.9-4.3atm	$=k[NH_3][Ar)$	15.62	41977	Shock Tube, Mass Spectroscopy	388
2300-3200K	Ne	0.3-1.4atm	$=k[NH_3][Ne]$	14.4	33211	Shock Tube, Mass Spectroscopy	389
2000-3000K	Ar	10-80atm	$=k[NH_3][Ar]$	15.76	38746	Shock Tube, UV Absorption	381
2300-3100K	Ar	0.3-2 atm	$=k[NH_3][Ar]$	15.76	38746	Shock Tube, UV Absorption	385
2200-2600K	Ar	20-300atm	$=k[NH_3]$	12.82	49314	Shock Tube, UV Absorption	385
Unimolecular Decomposition:							
2500-3000K	Kr	0.5 atm	$=k[NH_3][Kr]$	16.08	45791	Shock Tube, Mass Spectroscopy	390
1666-3333K	Ar	0.08-4.1atm	$=k[NH_3][Ar]$	16.25	46344	Shock Tube, UV Absorption	386
2200-3300K	Ar	0.2 atm	$=k[NH_3][Ar]$	16.60	47265	Shock Tube, UV Absorption	387
2200-3300K	Ar	50atm	$=k[NH_3]$	15.74	54240	Shock Tube, UV Absorption	387
2215-2750K	Ar	2.9-4.3atm	$=k[NH_3]$	14.0	42380	Shock Tube, Mass Spectroscopy	388
NH3 + H --> NH2 + H2:							
1667-3333K	Ar	0.08-4.1atm	=k[NH3][H]	14.10	11091	Shock Tube, UV Absorption	386
NH2 + H --> NH + H2:							
1667-3333K	Ar	0.08-4.1atm	-r[NH2]=k[NH2][H]	13.48	4307	Shock Tube, UV Absorption	386

However, Genich et al.[38] found an initial linear rather than parabolic rise for [NH] and gave the following expression:

$$d[NH]/dt = k'[NH_3]_0^2$$

This indicated that the chain mechanism (2-6.2) and (2-6.3) was incorrect.

Michael and Wagner[39] confirmed the presence of the radical NH but found that its low concentration precluded quantitative measurements. Furthermore, other species such as N_2H_3 were not detected. He considered that H atoms might play an important role and proposed the following mechanism:

$$NH_3 + H \dashrightarrow NH_2 + H_2 \qquad (2\text{-}6.4)$$

$$NH_2 + H \dashrightarrow NH + H_2 \qquad (2\text{-}6.5)$$

$$2NH_2 \dashrightarrow NH + NH_3 \qquad (2\text{-}6.6)$$

$$2H + Ar \dashrightarrow H_2 \qquad (2\text{-}6.7)$$

$$2NH \dashrightarrow N_2 + H_2 \qquad (2\text{-}6.8)$$

$$2NH_2 \dashrightarrow N_2 + 2H_2 \qquad (2\text{-}6.9)$$

He suggested that the difference between the observed activation energy for ammonia dissociation (about 83 kcal/mole) and the dissociation energy of the H_2N-H bond (about 102 kcal/mole) might be explained on the basis of energy contribution from a number of vibrational modes of the ammonia molecule.

Dove and Nip[381] found that the addition of H_2 decreased the removal of NH_3 and also suppressed NH, but left the NH_2 concentration relatively unchanged. They proposed a comprehensive mechanism in which NH_3 is removed by unimolecular decomposition and by attack by H, NH, and NH_2. They obtained the rate constant of the unimolecular decomposition of NH_3 by computer simulation. The values obtained are given in Table 2-6.1.

Yumura and Asaba[386] investigated the thermal decomposition of ammonia in a shock tube by monitoring the concentration of atomic hydrogen over the temperature range 1666-3333K. They found that the concentration profile of atomic hydrogen formed by decomposition of ammonia could be accounted for by reactions (2-6.1), (2-6.4), (2-6.5) and (2.6-10).

$$2NH \dashrightarrow N_2 + 2H \qquad (2\text{-}6.10)$$

They obtained the rate constants for reactions (2-6.1), (2-6.4), and (2-6.5) as listed in Table 2-6.1.

In the high pressure region (above 100 atm), the thermal decomposition of NH_3 changes reaction order from second to first[385,387]. The first-order rate constant was determined by Genich et al.,[385] and Holzrichter[387]. However, a large discrepancy exists between the results obtained as may be seen from Table 2-6.1.

(2). Catalytic Decomposition of NH_3 over Limestones

The decomposition of NH_3 over limestone (reaction (2-6.11))

$$2NH_3 \xrightarrow{Surface} N_2 + 3H_2 \qquad (2\text{-}6.11)$$

is important in the modelling of NO formation and destruction in fluidized bed combustion.[380] There are only two reports[355, 380] on the catalytic decomposition of NH_3 over calcined limestone.

Furusawa et al.[380] reported, in their fluidized bed combustor investigation, an expression of rate for reaction (2-6.11) over calcined limestones as

$$-r_{NH3} = k_{(2\text{-}6.11)}[NH_3]$$

with a rate constant at T = 1100K of $k_{(2\text{-}6.11)} = 30\ sec^{-1}$.

Lee et al.[355] also observed the catalytic effect of calcined limestone on the decomposition of NH_3 but no rate data was reported.

Further investigations of reaction (2-6.11) are needed for the analysis of NO and N_2O formation and destruction in fluidized bed combustion.

2-7. ARTIFACTS IN THE MEASUREMENT OF N_2O FROM COMBUSTION

Since the environmental effects of N_2O became a concern, field measurements of N_2O in large scale industrial combustors showed substanial N_2O emissions in systems fired with residual oil or coal (fuels that contain both nitrogen and sulfur)[8,393-395]. However, the characterization of N_2O emissions has become more complex due to the recent discovery of a major sampling artifact by Muzio and Kramlich[396]. Their work shows that in a natural gas flame initially containing 750 ppm NO (dry basis) but no sulfur species, the measured N_2O concentration was negligible (<3 ppm). However, when 1000-1500 ppm of SO_2 was added to the system, as much as 300 ppm N_2O was found by later analysis. Further tests show conclusively that most, if not all, of the measured N_2O was produced in the sample collection flask, which is similar to that used by most investigators measuring N_2O from combustion sources.

Their tests also showed that scrubbing SO_2 from the sample reduced the measured N_2O to 3 ppm, comparable to the value obtained when no SO_2 was initially present. Drying the sample in an ice trap reduced the measured N_2O to 26 ppm. They also showed that NO is converted into N_2O within the container by a reaction whose overall time constant is of the order of 2 hours. Each mole of NO appears to convert into as much as 0.40 mol of N_2O, depending on the conditions. The necessary reagents are NO, O_2, SO_2, and moisture at concentrations that are representative of coal combustion flue gas.

Lyon and Cole[397] proposed a mechanism to explain the observed N_2O production. The proposed mechanism involves the oxidation of NO to NO_2, followed by absorption into surface moisture or condensate, chemical reaction, and release as N_2O. i.e., in gas phase,

$$NO + NO + O_2 \dashrightarrow NO_2 + NO_2 \tag{2-7.1}$$

and in liquid phase,

$$2NO_2 + H_2O \dashrightarrow HNO_2 + HNO_3 \tag{2-7.2}$$

$$HNO_2 + HSO_3^{-1} \dashrightarrow NOSO_3^{-} + H_2O \tag{2-7.3}$$

$$NOSO_3^{-1} + H^{+}(+ H_2O) \dashrightarrow HNO + H_2SO_4 \tag{2-7.4}$$

$$NHO + HNO \dashrightarrow N_2O + H_2O \tag{2-7.5}$$

The present information implies that the artifact can dominate results from coal and oil flames, but not sulfur-free gas flames. The mechanism proposed by Lyon and Cole[397] was based on the early conclusion that reaction of NO_2 with sulphate ion ultimately produced N_2O[398]. However, this model predicts 50% more N_2O than observed, and they have not investigated the relationship between the formation of N_2O and the concentrations of NO, SO_2, and H_2O. Therefore they have little or no evidence to support the mechanism. Their experiments were carried out only at room temperature, no accurate measurements of the reaction rate have been made at various temperatures. One could question if NO conversion to N_2O in a mixture of $NO/SO_2/H_2O$ at increased temperatures occurs at significant rates. If so, it could be a possible pathway for N_2O formation in combustion processes in which fuels containing nitrogen and sulphur are used. The proposed mechanism excluded the possibility on the basis that there is no condensed water at higher temperatures. This supposition is worthy of investigation.

PART III. AREAS OF UNCERTAINTIES AND SUGGESTIONS FOR FUTURE STUDIES

A Comparison of N_2O destruction reactions (N_2O as a reactant), and N_2O formation reactions (N_2O as a product) leads to the conclusion that the later are less extensively investigated. Based on the discussion in this literature survey, we can identify important areas of uncertainty in the kinetic measurements of N_2O formation and destruction in combustion process which are worthy of further investigation.

The most important area in which large discrepancies exist is the information available on reactions of HCN and NCO. Kramlich et al.[9] suggested that if HCN appears in the gas phase between 1150K and 1500K, it will be partially converted to N_2O. They suggested that the source of HCN might be either direct devolatization, or a char gasification reaction and that the conversion of HCN to N_2O was through reactions (1-7.3),and (1-8.6).

$$O + HCN \dashrightarrow NCO + H \quad (1\text{-}7.3)$$

$$NCO + NO \dashrightarrow N_2O + CO \quad (1\text{-}8.6)$$

However, no unequivocal evidence exists to support the proposed mechanism for formation of HCN from fuel-N. The four published rate data for reaction (1-7.3) are in reasonable agreement in the temperature range 1500-2500, but values published in the low temperature range are about two orders of magnitude lower than values obtained by extrapolation of the high temperature data[199,200,202,204]. The only two rate data for reaction (1-8.6) are in good agreement with at 295K[205,210]. However, no high temperature rate data has been reported. Furthermore, the branching ratio of reaction (1-7.1),(1-7.2), and (1-7.3)

$$HCN + O \dashrightarrow CN + OH \qquad (1\text{-}7.1)$$

$$HCN + O \dashrightarrow NH + CO \qquad (1\text{-}7.2)$$

$$HCN + O \dashrightarrow NCO + H \qquad (1\text{-}7.3)$$

and the branching ratio of reaction (1-8.6), (1-8.7), and (1-8.8),

$$NCO + NO \dashrightarrow N_2O + CO \qquad (1\text{-}8.6)$$

$$NCO + NO \dashrightarrow N_2 + O + CO \qquad (1\text{-}8.7)$$

$$NCO + NO \dashrightarrow N_2 + CO_2 \qquad (1\text{-}8.8)$$

and the other NCO reaction channels, such as (1-8.2) and (1-8.3),

$$O + NCO \dashrightarrow NO + CO \qquad (1\text{-}8.1)$$

$$H + NCO \dashrightarrow NH + CO \qquad (1\text{-}8.2).$$

are fundamental in any assessment of the importance of the proposed mechanism for N_2O formation in combustion processes. This lack of data requires a systematic investigation of the reactions of HCN and NCO.

There is little data available to assist in evaluation of the catalytic effect of char, limestone, quartz, and $CaSO_4$ on the conversion of NO to N_2O. These investigations are necessary since these materials often represent in fluidized bed combustors.

The formation of N_2O by reduction of NO by various processes, such as, catalytic NO reduction by CO, catalytic reduction by NH_3, Thermal $DeNO_x$, etc., should be re-examined. It was reported that in the reduction of NO by CO over silica-supported Rh, the selectivity for N_2O formation is 76% to 81% in the temperature range of 498 to 500K.[274] Also it has been reported that production of N_2O is significant at T>500K in the reduction of NO with NH_3 on Al_2O_3- and TiO_2-supported metal oxide catalysts. These results indicate that N_2O formation through NO reduction might be an important contribution of the global increase in N_2O concentration. However, there is no systematic research on the formation of N_2O in these processes and no attention has been given to N_2O formation in the Thermal $DeNO_x$ process. The lack of experimental data on the selectivity of N_2O production with various catalysts, temperature effect on the selectivity, and mechanism of the N_2O production in these techniques, hampers an evaluation of the importance of these reactions.

The reactions in the mixture of $NO/SO_2/H_2O/O_2$ were investigated as to explain the artifact in the measurement of N_2O.[396,397] However, previous investigations have been only carried out at room temperature and no report on the effect of the phase of H_2O is available. No information is available on the possible conversion of NO to N_2O in a mixture of $NO/SO_2/H_2O/O_2$ at increased temperature. If such conversion occurred, it could be a possible pathway for N_2O formation in combustion of fuels containing nitrogen and sulphur. The proposed mechanism excludes this possibility on the basis that there is no condensed water at higher temperatures, However, this needs to be clarified.

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